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THE CHEMICAL ANALYSIS OF THE APPLE AND SOME OF ITS PRODUCTS.

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IN the Fall of 1899, the writer was called upon, by the Pennsylvania Department of Agriculture, to make a chemical study of the apple and its various products. The results of this investigation have been embodied in Bulletin No. 58 of the Department's publications. For the complete tabulation of all the analyses made in connection with this work, together with the discussion of the results, reference is made to the above bulletin. A brief summary of the results is presented,[1] however, in this connection, preliminary to a more complete description of the methods of analysis employed. The latter, in fact, is the main purpose of the present paper, inasmuch as no description of methods was included in the original bulletin. The methods herein described, while designed especially for the examination of apples and apple products, have been used successfully in a few other instances, and the writer believes that, with a few modifications perhaps, they could be employed in the analysis of any of our common fruits.

[1] This is done with the kind permission of Prof. John Hamilton, secretary of the Pennsylvania Department of Agriculture.

COMPOSITION OF APPLES.

	Water.	Reducing sugars.	Sucrose.	Starch.	Ash.	Acid as malic.	Marc.
Unripe apples (2 analyses)	80.67	6.43	2.84	3.92	0.27	1.14	....
Summer apples (6 analyses)	85.00	7.10	3.36	1.04[1]	0.28	0.68	....
Winter apples (21 analyses)	83.16	8.16	4.16	....	0.26	0.59	1.85[2]

The above analyses represent simply the composition of the edible or fleshy portion of the apple. These figures, together with other determinations made upon the combined pulp and marc from different varieties of fruit, have furnished the following table:

APPROXIMATE AVERAGE COMPOSITION OF THE FLESH OF THE RIPE APPLE.

Ingredient.	Per cent.
Inorganic.	
Water	84.00
Ash	0.30
Organic.	
Sugars:	
Reducing sugars	8.00
Sucrose	4.00
Starch	0.00
Marc:	
Cellulose	0.90
Pentosans	0.50
Lignin	0.40
Organic acids:	
Free acid as malic	0.60
Combined acid as malic	0.20
Pectin bodies	0.40
Crude fat	0.30
Protein	0.10
Undetermined (tannin, etc.)	0.30
	100.00

THE CHEMICAL COMPOSITION OF APPLE ASH.

Ingredient.	Per cent.
Potash	55.94
Soda	0.31
Lime	4.43
Magnesia	3.78
Ferric oxide	0.95
Alumina	0.80
Chlorine	0.39
Silica	0.40
Sulphur trioxide	2.66
Phosphorus pentoxide	8.64
Carbon dioxide	21.60
	99.90
Deduct oxygen equivalent to chlorine	0.09
Total	99.81

[1] One analysis.

[2] Eight analyses.

The above analysis was made upon the combined ashes from many different varieties of apples, the flesh of the fruit being the only part taken for incineration.

COMPOSITION OF APPLE JUICES.

	Specific gravity.	Solids.	Reducing sugars.	Sucrose.	Free acid as malic.	Ash.	Pectin.	Albuminoids.	Rotation Ventzke 400 mm. tube.
Juice from summer apples (5 analyses)	1.0502	12.29	6.76	3.23	0.72	0.29	0.12[1]	0.03[1]	— 26.67
Juice from winter apples (4 analyses)	1.0569	13.96	8.57	3.40	0.43	0.27	0.12[2]	0.02[2]	— 45.15

The composition of other fruit juices, from analyses made by the writer, is given for purposes of comparison.

Kind of juice.	Specific gravity.	Solids.	Reducing sugars.	Sucrose.	Free acid as malic.	Ash.	Pectin.	Albuminoids.	Rotation Ventzke 400 mm. tube.
Strawberry	1.0420	9.64	5.90	0.89	1.28	0.61	0.63	0.38	— 5.28
Red raspberry	1.0463	11.01	5.13	2.31	1.44	0.60	0.88	0.75	+ 7.32
Black raspberry	1.0567	13.65	9.52	...	1.85	0.60	0.72	0.38	— 25.20
Black cherry, very sweet	1.1034	24.30	16.35	...	1.47	0.79	0.30	0.63	— 29.80
Red cherry, sour	1.0461	11.22	7.33	...	1.32	0.57	0.25	0.56	— 12.96

Closely related to apple juice is what is known as "second pressings", used so extensively at present for jelly-making and vinegar stock. It is made simply by wetting apple pomace with water and repressing.

COMPOSITION OF SECOND PRESSINGS.

Specific gravity	1.0376
Rotation Ventzke 400 mm. tube	— 31.94
	Per cent.
Solids	9.14
Reducing sugars	6.87
Sucrose	1.49
Ash	0.20
Undetermined (pectin, malic acid, etc.)	0.58

The composition of completely fermented cider and vinegar is

[1] Four analyses.

[2] One analysis.

shown by the following figures, compiled from analyses made upon samples of known purity.

COMPOSITION OF CIDER AND CIDER VINEGAR.

	Specific gravity.	Solids.	Ash.	Reducing sugars.	Acetic acid.	Malic acid.	Alcohol.	Pectin.	Albuminoids.	Rotation Ventzke 400 mm. tube.
Cider (6 analyses)	1.0006	2.34	0.29	0.32	0.61	0.25	5.51	0.04	0.02	—2.34
Vinegar (4 analyses)	1.0184	2.00	0.44	0.52[1]	6.19	0.14	none	0.17	0.01	—2.01[1]

COMPOSITION OF MISCELLANEOUS APPLE PRODUCTS.

	Moisture.	Reducing sugars.	Sucrose.	Ash.	Free acid as malic.	Albuminoids.	Pectin.	Marc.
Evaporated apples (2 anal.)	27.61	32.80	19.02	1.10	4.08	0.87	...	5.53
Apple butter (1 anal.)	52.58	37.20	1.14	0.97	2.52	0.25	2.15	1.14
Cider jelly (1 anal.)	44.53	49.50	2.18	1.39	3.61	...	1.60	none
Apple pomace (1 anal.)	70.76	8.09	2.40	0.49	...	1.25	...	...

METHODS OF ANALYSIS.

The methods employed in making the determinations contained in the preceding tables are in many cases simply the ordinary processes described in most books on commercial or agricultural analysis. The methods[2] of the official agricultural chemists were employed as far as possible. Only such departures, from the usual methods as it was found advisable to make, will be described.

[1] The writer desires at this point to call attention to a statement made by Doolittle and Hess in a recent number of this Journal (**22**, 219). It is said that "the solids of pure cider vinegar give no rotation with the polariscope, and little or no reducing action on Fehling's solution after the customary clarification with lead acetate." This is certainly a mistake. Of the many samples of pure cider vinegars examined by the writer at the Pennsylvania Experiment Station during the past four years, not one has failed to give a decided rotation to the left, when examined in the 400 mm. tube of the polariscope; likewise all have appreciably reduced Fehling's solution, whether previously clarified with animal charcoal or lead subacetate.

An unpublished experiment conducted by the writer at this Experiment Station shows that levulose is the only sugar present in properly fermented cider vinegar, the sucrose and dextrose having both disappeared in the course of the alcoholic fermentation. The acetic fermentation, which sets in before the last traces of levulose have been destroyed, seems to prevent the complete removal of the sugar by alcoholic fermentation, and the percentage of levulose continues, thereafter, nearly constant.

[2] Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry.

Determination of Moisture and Solids.—This, apparently the most simple of all analytical processes, was found at the outset of the work to offer the greatest difficulties. The methods ordinarily prescribed recommend that the material be dried at 100° C., or even higher, until a constancy in weight is attained. In making determinations by any of these methods the writer has found it impossible to obtain any such constancy in weight; the residue would continue to lose, until its percentage became finally much less than the sum of the percentages of the different solid constituents. A decomposition of some kind was indicated and the unreliability of drying at a high temperature clearly shown.

The difficulty experienced is undoubtedly due to a breaking-up of the sugars of the fruit, principally levulose. This has been found true in the case of other bodies containing levulose, as has been shown by Carr[1] and Sanborn in their experiments upon "the dehydration of viscous organic liquids." These writers, after making "upward of 5,000 separate determinations, ranging over all the better-known methods and covering such materials as pure sugar and levulose solutions, honey, molasses, molasses "flowers," sorghum, beet and maize juices, etc., etc," "conclude that it is impossible to dehydrate, quantitatively, solutions containing levulose without the occurrence of decomposition, if the temperature be 100°, the environment air, and the pressure equal to that of the atmosphere." The method finally adopted by Carr and Sanborn, to prevent this decomposition of levulose during dehydration, consists in drying the material on pumice stone in flat-bottomed dishes, at 70° C. and a vacuum of 25 inches.

The writer has been unable to find any work relating to the dehydration of fruits, or the products therefrom, *in vacuo*, but the same necessity would exist for such dehydration as with other levulose-containing materials, the presence of levulose in most fruits being sufficiently indicated by the marked levorotation, which the clarified juices give to the plane of polarized light.

In the various analyses, previously recorded, the writer effected dehydration in most cases by drying the material at 70° C. in a vacuum as recommended by Carr and Sanborn, using, however, perforated brass or copper tubes filled with asbestos for absorbing the liquid, instead of pumice stone in dishes as in the method of the above authorities.

[1] Bulletin 47, U. S. Department of Agriculture, Division of Chemistry, p. 134. See also this Journal, p. 17, (23) of proceedings.

The perforated tubes employed measured 9 cm. long by 2 cm. in diameter. In the case of liquids, fruit juices, cider, vinegar, etc., the tubes are nearly filled with freshly ignited asbestos,—the latter being tightly packed with a rod against the sides in the upper half of the tube, thus leaving a central cavity extending part way into the asbestos. Each tube thus prepared is placed into a glass-stoppered weighing-bottle of sufficient size, and the whole weighed. About 5 cc. of the liquid to be analyzed are then delivered from a pipette into the cavity in the asbestos, the object of the cavity being to secure a rapid absorption, and even distribution of the liquid through the asbestos. The weighing-bottle is then immediately stoppered and reweighed, the increase in weight being the amount of substance taken. After removing the stopper, the bottle, together with the inner tube, is conveyed to a vacuum drying apparatus, where it is dried in an upright position, at a constant temperature of 70° C. During the first few hours of the drying, a slight current of air is drawn through the vacuum compartment, in order to remove the large excess of moisture at first given off. In the last stages of the drying the air current is decreased, and the vacuum kept at about 25 inches. Eight to ten hours are generally sufficient to secure complete dehydration; at the end of this time the weighing-bottle is removed from the oven, placed in a desiccator and, when cold, restoppered and weighed.

The bottles are then replaced in the oven and dried for a second period of a few hours to ascertain if constant weight has been secured. The first drying, however, has generally been found sufficient. A longer drying of several days has been found to produce no change in weight, when once dehydration was secured, showing that no decomposition of levulose is produced.

In determining moisture or solids in apples and other fruits the same method is employed, with the exception that the perforated tubes are filled only about one-fourth with asbestos. The grated pulp of the fruit to be analyzed is well sampled and mixed, and a small portion of 5 to 10 grams transferred through a short-necked funnel into the tube, when the bottle is restoppered and weighed. The drying is conducted as previously described; the slight amount of liquid, which sometimes oozes out into the weighing-bottle, does no harm.

In drying fruit products of much consistency, such as jelly, it

is best to dissolve a weighed amount of the material in water, before adding to the asbestos, in order to secure a better absorption. The same necessity of drying *in vacuo* at low temperature exists with evaporated fruit products, such as dried apples. In such cases the use of the inner perforated tube is dispensed with altogether. The finely cut material is weighed out directly in the weighing-bottle and the process conducted as already described.

It might be supposed that, with fermented ciders and vinegars, owing to the disappearance of levulose during fermentation, a determination of the solids by the vacuum method at 70° C. and by drying at 100° C. in the usual way would show no decided difference. Such, however, is not the case with completely fermented ciders and vinegars; a constancy in weight is attained by drying at 100° C., but the percentage of solids is invariably less than that obtained by the vacuum method. The following is an example of this; the experiment was performed upon a pure cider vinegar.

	Per cent.	
	I.	II.
Solids by drying at 100° C., two days.....	1.48	1.50
Solids by drying at 100° C., three days	1.47	1.49
Solids by drying *in vacuo* at 70° C., two days	3.29	3.39
Solids by drying *in vacuo* at 70° C., three days....	3.28	3.39

The percentage of reducing sugar was only 0.16 per cent. so that decomposition of levulose does not explain the discrepancy. It may be due partly to the volatilization of glycerol, which is formed during the alcoholic fermentation. Indications, however, point to the presence of other substances, besides levulose, in fruit products, which are decomposable at 100° C.

The Calculation of Solids in Fruit Juices from the Specific Gravity.—The application of this principle, by means of the Brix spindle, in the analysis of juices from the beet and sugar-cane is too well known to require mentioning; it has also been applied by Kulisch[1] in the analysis of apple juices, the degrees Brix or Balling, corresponding to the specific gravity of the juice at 17.5° C., being the percentage of solids. The writer has compared this method of estimating solids with the actual determination, and the agreement has usually been very satisfactory. Instead of using degrees Brix the solids of juices may be calculated from the formula $245\ (S-1)$, S being the specific gravity of the

[1] "Landwirthschaftliche Jahrbücher, **19**, 110 (1890).

juice at 17.5° C. Such methods of estimating solids are, of course, only applicable in the case of fresh juices, before the beginning of the alcoholic fermentation. The following table gives the percentage of solids, as estimated and actually determined in a number of different juices.

No.	Kind of juice.	Specific gravity 17.5° C.	Degrees Brix.	Solids by formula 245 (*S*—I). Per cent.	Actual solids at 70° C. *in vacuo*. Per cent.
1	Apple juice (second pressing)	1.0376	9.39	9.21	9.14
2	" "	1.0474	11.73	11.61	11.36
3	" "	1.0481	11.90	11.78	11.81
4	" "	1.0484	11.97	11.86	11.87
5	" "	1.0488	12.07	11.96	11.71
6	" "	1.0517	12.75	12.67	12.78
7	" "	1.0525	12.94	12.86	12.77
8	" "	1.0539	13.26	13.21	13.29
9	" "	1.0559	13.73	13.70	13.94
10	" "	1.0560	13.76	13.72	12.83
11	" "	1.0568	13.94	13.92	13.84
12	" "	1.0613	14.99	15.01	14.90
13	" "	1.0722	17.50	17.69	16.82
14	Strawberry juice.....	1.0420	10.44	10.29	9.64
15	Red raspberry juice.....	1.0463	11.47	11.34	11.01
16	Black raspberry juice.....	1.0567	13.92	13.89	13.65
17	Red cherry juice.....	1.0461	11.42	11.29	11.22
18	Black cherry juice.....	1.1034	24.42	25.33	24.30
	Average.....	.....	13.42	13.41	13.16

The formula, as a rule, gives results slightly closer to the actual percentage of solids, except in case of juices of very high gravity, as No. 18 of the preceding table. The difference between actual and calculated results rarely exceeds 0.2 or 0.3 of a per cent.; there is occasionally, however, a notable discrepancy as in the case of apple juices Nos. 10 and 13. Calculating the solids from the gravity of a juice is sufficiently accurate for many purposes; such an estimation is preferable, in any case, to the old method of determining solids by drying at 100° C.

Ash.—This was determined according to the official method, about 20 grams of material being taken for analysis. In incinerating large quantities of material, to obtain ash for the ash analysis, it is necessary to exhaust the charred mass first with water. The insoluble residue is collected on a filter, burned, and this ash added to the residue left on evaporating the aqueous extract. The whole is then heated to a low redness till the ash is white.

Reducing Sugar.—This was calculated, in the various analyses given, simply as invert sugar. Strictly speaking this is not correct, for the dextrose and levulose of fruit juices are present in, by no means, equal proportions, as in apple juices where the percentage of levulose is nearly double that of dextrose. Nevertheless, when these sugars are not separately determined, it has seemed to the writer more accurate to consider the reducing sugar as invert rather than dextrose or levulose alone. The invert sugar is calculated from the weight of reduced copper according to the tables of Meissl and Wein ; such small amounts of sucrose, as are present in fruit juices, do not affect the accuracy of the determination.

In the determination of reducing sugar in fruit juices, 20 cc. of the filtered juice are measured out into a 500 cc. flask, about 300 cc. of water are added, and, after neutralizing carefully with sodium hydroxide using phenolphthalein, the volume is completed to the mark. Twenty-five cc. of this solution (1 cc. of original liquid) are taken for the copper reduction. The reduced cuprous oxide is filtered in asbestos tubes and, after drying, reduced in a current of hydrogen, and the weight of copper determined. In case of partly fermented juices larger amounts of liquid can be used for dilution. With completely fermented ciders and vinegars, which contain but very little sugar, the liquid after neutralizing needs little if any dilution. In calculating the percentage of reducing sugar, it is, of course, necessary to take into account the specific gravity of the liquid analyzed.

In determining reducing sugar in apples and other whole fruits the following method was adopted : 100 grams of the grated pulp are washed on a muslin filter in a large funnel, with repeated quantities of cold water, the filter being squeezed after each addition of water to hasten the removal of the sugar. The filtrate is caught in a 2-liter flask, and the washing continued until the liquid is nearly up to the mark. After completing the volume, the flask is shaken, and 200 cc. (10 grams of fruit) of the filtered solution are transferred to a 250 cc. flask ; this solution is neutralized with soda as before and the volume made up to 250 cc. from which 25 cc. (1 gram of fruit) are taken for the copper reduction.

The same method is used with evaporated fruit products, as with whole fruit, except that a smaller amount of material is taken for analysis. Twenty-five grams of the finely cut material

are treated with 200 cc. of water for several hours in a large beaker until the substance has swollen to a soft pulp. The material is then brought upon the muslin filter, and washed to 2 liters as before.

With fruit jellies, 10 grams of the material are dissolved in water, neutralized, and made to 1 liter.

Sucrose.—This was determined in the majority of cases from the increase in the copper-reducing power, after inversion with hydrochloric acid. In making the analysis the method of procedure is as follows:

The same amount of solution (juice, aqueous extract of fruit, etc.) is taken as in the determination of the reducing sugars; one-tenth its volume of concentrated hydrochloric acid is added, and the flask placed in a water-bath at 70° C. The contents of the flask, after reaching a temperature of 67°–70° C., are kept within this limit for exactly five minutes when the solution is cooled, neutralized, and made up to the same volume as in determining reducing sugars. Twenty-five cc. of this solution are taken for the copper reduction, the calculation being made to invert sugar as before. The difference between the percentage of invert sugar before and after inversion, multiplied by 0.95, will give the percentage of sucrose.

Sucrose has also been determined in fruit juices by means of the polariscope. 52.096 grams of juice are made to 100 cc. Fifty cc. of this solution are clarified with 5 cc. of lead subacetate, and the reading taken in the 200 mm. tube at about 20° C. The remaining 50 cc. are inverted with 5 cc. of concentrated hydrochloric acid, as described above, cooled rapidly and diluted to 100 cc. The reading is taken in the 200 mm. tube, at the same temperature as the first solution, clarifying, if necessary, with animal charcoal. The first, or direct reading increased by 0.1 and divided by 2 $= a$, the invert reading $= b$, $100\frac{(a\ b-)}{142.4 - \frac{t}{2}} =$ percentage of sucrose, t being the temperature of the solutions at time of reading.

Levulose and Dextrose.—In many cases a separate determination of these sugars has been made. Several courses of procedure have been followed according to conditions.

In the presence of both dextrose and sucrose, the levulose was determined by the difference in polarization of the solutions at widely separated temperatures.[1] With juices, etc., the pure liquid is first clarified by means of animal charcoal, and the polariscope reading taken in a 200 mm. tube, first at about 15° C. (v) and then at about 85° C. (v'). The tube used should be provided with a metal jacket, through which water of the desired temperature is allowed to circulate. The percentage of levulose l is calculated from the formula

$$l = \frac{v - v'}{G(t \times -0.0323)};$$

$v - v'$ = the algebraic difference between the two readings and, if levulose is present, will always be a minus quantity, owing to the fact that the rotation of levulose solutions when heated is deflected towards the right.

G = the specific gravity of the liquid.

t = the difference in temperature between the readings.

The value -0.0323[2] represents the deviation (Ventzke), for each degree centigrade difference in temperature, produced by 1 gram of levulose in 100 cc.

With fruit jellies, etc., a definite weight of the material (20 to 50 grams) is dissolved in 100 cc. of water and the solution, after clarifying, polarized at different temperatures as before. In this case the percentage of levulose, or l, $= \frac{100\ (v - v')}{W(t \times -0.0323)}$, W being the grams of substance in 100 cc.

Knowing the percentage of levulose, and the copper-reducing power of the solution, the percentage of dextrose admits of calculation. Volumetric determinations by Soxhlet upon solutions of invert sugar have shown that for the same volume of Fehling's solution reduced, 1 part of levulose corresponds to 0.924 part of dextrose. Gravimetric determinations made by the writer upon pure solutions of invert sugar show a ratio somewhat lower than this, as the following table shows. The gravimetric method of Allihn was followed:

[1] See Wiley's "Agricultural Analysis," Vol. III, pp. 267–273.

[2] This figure was deduced from the general formula of Jungfleisch and Grimbert which gives the specific rotatory power of levulose for any temperature or concentration. The equation is $[\alpha]_D = -[101.38 - 0.56\,t + 0.108\,(c - 10)]$, in which t is the temperature of the solution and c the grams of levulose in 100 cc. See Landolt: "Das optische Drehungsvermögen, 2 Auflage, p. 524.

1 Weight of sucrose taken. Gram.	2 Weight of invert sugar therefrom. Gram.	3 Weight of copper. Gram.	4 Corresponding weight of dextrose (Allihn's table). Gram.	5 Ratio of dextrose to invert sugar.
0.2300	0.2421	0.4315	0.2313	1.047
0.1533	0.1614	0.2950	0.1538	1.049
0.1150	0.1211	0.2230	0.1148	1.055
0.0575	0.0605	0.1120	0.0570	1.061

It is seen that the ratio of dextrose to invert sugar increases slightly as the concentration of the solution diminishes; the variation, however, is not sufficient to make any appreciable difference in the calculations. Taking the average of the above determinations, 1 part of dextrose could correspond to 1.053 parts of invert sugar for the same weight of copper reduced. Since invert sugar is made up of equal parts of dextrose and levulose, 1 part of dextrose would correspond to 1.106 parts of levulose for the same amount of reduced copper, or 1 part of levulose would equal 0.90 part of dextrose.

Knowing the percentage of levulose the percentage of dextrose (d) may be found from the formula

$$d = D - 0.9\,l,$$

where D = percentage of reducing sugar as dextrose (Allihn's method), and l = percentage of levulose as found by polarization.

In the absence of sucrose the writer has calculated the percentages of dextrose and levulose from the rotation and copper-reducing power. The factors necessary to know are P, the specific rotatory power, and D, the percentage of reducing sugars as dextrose.

To determine the specific rotatory power it is necessary to know the rotation of a known amount of the sample in a tube of definite length. For this purpose in the case of fruit juices, etc., it is best to read the clarified liquid directly in a 400 mm. tube; with more concentrated products 20 grams of substance are dissolved in water and made to 100 cc. For clarification the writer has used animal charcoal in the majority of cases, though lead subacetate answers equally well and in some cases is found necessary. But very little difference has been noticed in the rotation by these two methods of clarification, provided excess of lead solution is avoided. In clarifying with lead the polariscopic reading must, of course, be corrected for the dilution. In case of a sugar polariscope with a Ventzke scale, the reading must be corrected to angular degrees by multiplying by the factor 0.3468.

The formula for calculating the specific rotatory power in the case of liquids is

$$P(20^\circ\text{ C.}) = \frac{0.3468\,v}{4G}.$$

v = polariscopic reading, Ventzke scale, in 400 mm. tube at 20° C.

G = the specific gravity of the solution.

4 = the length of the tube in decimeters.

If the material is weighed out and made up to 100 cc. by dilution with water, the formula becomes

$$P(20^\circ\text{ C.}) = \frac{0.3468\,v}{4W} \times 100,$$

W being the grams of substance taken.

The specific rotatory power of a solution being dependent upon the percentages and specific rotatory powers of its ingredients, we would have for solutions containing dextrose and levulose alone, the formula

$$53\,d - 90\,l = 100\,P.$$

d and l are the percentages of dextrose and levulose, and 53 and — 90 are their respective specific rotatory powers, at 20° C., the concentration for each sugar not exceeding 10 per cent.

Substituting the formula $d = D - 0.9\,l$ in the previous equation we obtain :

$$l = \frac{53\,D - 100\,P}{138}$$

As far as the writer has been able to compare them, these two methods of determining levulose have shown a very close agreement, as the following example, in the case of a partly fermented cider, will illustrate.

Specific gravity of cider = 1.0067 = G.

Rotation of cider at 15° C., 200 mm. tube, Ventzke scale = — 10.1° = v.

Rotation of cider at 85° C., 200 mm. tube, Ventzke scale = — 5.5° = v'.

The difference in temperature of the two readings = 70 = t.

Substituting these values in the formula

$$l = \frac{v - v'}{G(t \times -0.0323)},$$

we find l = 2.04 per cent.

The percentage of reducing sugars as dextrose was $2.26 = D$.

The rotation of the cider at 20° C., 400 mm. tube, Ventzke scale, $= -18.8° = v$.

The specific rotatory power of the cider from the formula

$$P(20° \text{ C.}) = \frac{0.3468\, v}{4G},$$

is therefore $-1.62 = P$.

Substituting the above values for D and P in the equation

$$l = \frac{53D - 100P}{138},$$

we find $l = 2.04$ per cent., the same as before.

The percentage of dextrose in the cider, calculated from the formula $d = D - 0.9l$, is 0.42 per cent.

Starch.—This substance has been found in all green pomaceous fruits; it no doubt occurs in other classes of fruits in the early periods of their growth, though this is a point which has not been as yet fully investigated. In the ripening of fruits the starch is gradually converted into sugar, and this process continues even after picking until no vestige of starch remains. A determination of starch is, of course, only necessary when its presence is indicated by the iodine reaction.

The estimation of starch in fruits, depending as it does upon its conversion into dextrose, offers special difficulties, owing to the large amount of reducing sugars present, and the first step in any process of analysis must consist in the removal of all the sugars before the conversion of the starch is attempted. The process usually recommended consists in washing a weighed amount of the pulp either directly upon a filter, or by decantation upon the same, until all the sugars are removed. This method of procedure has been found by the writer to be extremely tedious, owing to the large amount of washing required and to the tendency which the pectinous and gummy matters of the fruit have of clogging the filter.

The following process adopted by the writer avoids in great measure this difficulty and, as it is carried out directly in connection with the sugar determination, effects a considerable saving of time.

100 grams of the finely-grated pulp are washed upon a muslin filter with repeated quantities of cold water, until the filtrate

amounts to 2 liters; the muslin is squeezed after each addition of water, as already described under the determination of sugar. In this way practically all of the starch is washed out of the pulp. The filtrate, after being well mixed, is transferred to a tall beaker or cylinder, where it is covered and allowed to stand in a cool place over night. The finely suspended particles of starch will have completely settled by this time to the bottom of the vessel, forming a compact mass. The liquid above the starch is then removed by means of a siphon or decantation down to within a short distance of the precipitate; this solution may be used for the determination of sugars and malic acid.

The precipitate of starch is transferred with small quantities of cold water to a hardened filter-paper and washed to remove the last traces of sugar: 100 cc. of water are usually sufficient for this. The starch thus prepared consists of a white crumbly mass, but is not perfectly pure, owing to the presence of some cellular and albuminoid matter. The starch might be determined at this stage with sufficient accuracy by direct inversion with hydrochloric acid as in the Sachsse method, but the writer has preferred to use the more exact process of first hydrolyzing with diastase.

A starch determination by means of the diastase method should also be made upon the residue left on the muslin filter after the washing, in case the latter should show any reaction with iodine. The writer has never found the residues to yield more than 0.1 or 0.2 per cent. of starch upon the original pulp, so that the determination is rarely necessary if the washing has been properly performed.

The official diastase method[1] was followed throughout, except as regards the neutralization after the inversion with hydrochloric acid. The writer has always preferred a 10 per cent. solution of sodium hydroxide, using phenolphthalein, instead of sodium carbonate as prescribed in the official method; the troublesome frothing incident to the use of the latter substance is thus avoided.

Marc.—This represents that part of the fruit, which is insoluble in water. It is best found in connection with the sugar determination; the residue left upon the muslin filter after the

[1] Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry.

washing, is transferred to a dish and dried to a constant weight at 100° C. With the exception of a trace of ash and albuminoid matter, the marc of apples was found to consist almost wholly of cellulose, lignin, and pentosans.

In case the percentages of the different marc constituents are desired, the pentosans are best determined by distilling a weighed amount of the dry marc with successive quantities of 12 per cent. hydrochloric acid, and precipitating the furfurol in the distillate by means of phloroglucin.[1] The cellulose is separated from the other marc constituents by the chlorination process of Cross and Bevan.[2] The lignin[3] bodies are estimated by the difference between the cellulose and pentosans and total marc, after correcting for the slight quantities of ash and albuminoid matter.

Malic and Acetic Acids.—No attempt was made by the writer to separate the various fruit acids in the analyses previously tabulated. The free acid was determined in every case by titration with decinormal soda, and calculated to malic acid. Besides the free organic acid, a considerable amount of the fruit acids exists in a combined form ; the amount of this can be estimated from the alkalinity of the ash. In case of ciders and vinegars, where acetic acid is present, the latter is first removed by steam distillation, and determined by titration with decinormal soda solution ; the distillation should be continued until 50 cc. of the distillate shows a neutral reaction. The solution left in the flask after the steam distillation is then titrated and calculated to malic acid as before.

Pectin.—This was determined by evaporating a definite amount of the fruit extract, juice, etc., to a small volume and precipitating with a large excess of 95 per cent. alcohol. After standing over night the precipitate was collected in a Gooch crucible, and washed with alcohol to remove all sugar. The precipitate was then dried at 100° C. to constant weight, and after incineration the weight of ash deducted and the loss estimated as pectin.

Other ingredients given in the preceding tables, such as fat, protein, etc., were determined according to the official methods of the agricultural chemists, and require no special description.

[1] For full description of the phloroglucin method for pentosans, see Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry, p. 25.

[2] Cross and Bevan: "Cellulose," p. 95.

[3] See article by Sherman : This Journal, 19, 305.

THE IDENTIFICATION AND PROPERTIES OF α- AND β-EUCAINE.[1]

By Charles Lathrop Parsons.

Received September 24, 1901.

TWO new alkaloids under the names α-eucaine and β-eucaine have recently been offered to the medical and dental professions for use as a local anesthetic. There is scarcely a reference to either in any strictly chemical journal but their use and physiological properties have been very fully discussed in medical and pharmaceutical publications. Although they are proprietary drugs the fact that β-eucaine is so often substituted for cocaine, in dental preparations, hay fever remedies, and other proprietary medicine, makes it highly desirable that their distinctive properties be carefully studied and that methods be found for their identification and separation from cocaine and other alkaloids. It was owing to the fact that I was called upon to analyze a special dental preparation containing eucaine that my attention was first called to the existence of the alkaloid, and I was greatly handicapped by the silence of chemical literature upon the subject.

α-Eucaine was first obtained by George Merling[2] by synthesis from triacetonamine through triacetonamincyanhydrin to triacetonalkamincarbonic acid, which, by the action of benzoyl chloride and subsequent action of methyl iodide in caustic potash solution, becomes *n*-methylbenzoyltetramethyl-γ-oxypiperidincarbonic acid methylester or "α-eucaine". This, when treated with hydrochloric acid, acts like other alkaloids forming a hydrochloride, in which form it is prepared and sold.

β-Eucaine was discovered by Albrecht Schmidt and George Merling[3] and was obtained by purifying the vinyldiacetonalkamine of Fischer[4] and substituting a benzoyl group for the hydrogen atom of the hydroxyl. Thus "β-eucaine" or benzoylvinyldiacetonalkamine, is also an alkaloid which, when treated with hydrochloric acid, forms the hydrochloride.

It will be seen from the structural formulas of α- and β-eucaine

[1] Read at the Denver meeting of the American Chemical Society, August 29, 1901.

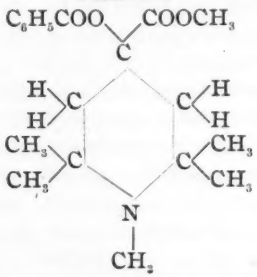
[2] *Apoth. Ztg.*, (1896), p. 293, 418, 448.

[3] Virchow's *Archives fur path. Anat. und Phys.*, (1896), vol. 145.

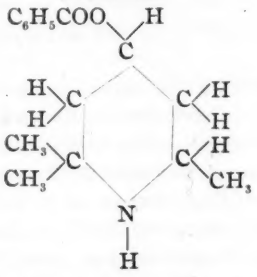
[4] *Ber. d. chem. Ges.*, 17, 1894.

that they have a close relation to cocaine and to tropacocaine.

α-Eucaine.



β-Eucaine.



It was this close chemical connection which led to the belief that they would show similar anesthetic properties.

It is not the purpose of this paper to enter into a discussion of the physiological and therapeutic effects of the eucaines but it is not out of place to state that the chief claims of their superiority over cocaine are that they are far safer to use, that they cause no excitation of the heart's action, that β-eucaine, especially, is some four or five times less toxic, that they have equal analgesic power with cocaine, that they do not decompose by boiling and their hydrochlorides can hence be easily sterilized, and that their solutions will keep for an indefinite time without decomposition. The quite extended use of β-eucaine would seem to show that many of these claims have been substantiated. It would be well to add that α-eucaine has at times an irritating action or smarting effect of its own before anesthesia sets in, which has rendered its acceptance and use somewhat doubtful. It is claimed that this is absent with β-eucaine or at least is no more often the case than with cocaine. β-eucaine is the one that is almost exclusively used and the firm which manufactures both furnishes only β-eucaine when "eucaine" alone is called for. Accordingly almost all preparations on the market consisting in part of eucaine contain β-eucaine hydrochloride and the question of analysis would generally be a distinction between this salt and cocaine.

To establish means of identification of eucaine, all the well-known reactions of the alkaloids have been tried and I have endeavored to find new ones applicable to this particular case.

In general the properties of the eucaine alkaloids follow those of the strychnine group and especially do they very closely

resemble cocaine. The bases themselves are readily soluble in benzene, chloroform, ether, chloroform-ether, petroleum ether or gasoline, and amyl alcohol. They can be easily extracted from their salts by rendering their solutions in water slightly alkaline with ammonia and shaking out with any of the above solvents. This extraction is, however, most rapidly accomplished with light petroleum distillates or with ether. α-Eucaine melts at 103°, β-eucaine at 91°, and cocaine at 98°. In following out any scheme of analysis of the alkaloids they will probably always be found where cocaine would be expected and their identification becomes essentially a separation from each other and cocaine. α- and β-eucaine are sold in the form of their hydrochlorides and it is upon this salt that most of the tests for their identification should be made. As usually prepared, α- and β-eucaine hydrochlorides are white powders, identical in appearance. They are, however, easily crystallizable.

α-Eucaine hydrochloride melts at about 200° C. and decomposes at the same time. It is soluble at ordinary temperatures in about ten times its weight of water, solubility varying with temperature. It is more soluble in hot water, from which it crystallizes out to an approximately 10 per cent. solution on cooling. It is soluble in about its own weight of alcohol, 10 grams requiring from 8 to 9 grams of alcohol for solution. It is but slightly soluble in ether or olive oil, but glycerol dissolves it much the same as water.

β-Eucaine hydrochloride melts at 268° C. with decomposition. At ordinary temperatures it is soluble in water to the extent of about 3 per cent., but is more than twice as soluble in hot water from which most of the excess crystallizes slowly after cooling. Its solubility in alcohol is greater than in water or about 11 per cent., varying somewhat with the temperature. This comparative insolubility is one of its chief characteristics especially differing from cocaine hydrochloride which dissolves in less than its own weight of either water or alcohol. It is almost insoluble in ether or olive oil.

REACTIONS IN WHICH THE HYDROCHLORIDES OF α-EUCAINE, β-EUCAINE AND COCAINE ACT ALIKE.

Mayer's reagent gives with either α- or β-eucaine a light yellowish amorphous precipitate.

Wagner's reagent gives a voluminous reddish brown precipitate even in dilute solutions.

Tannic acid (1 : 10) gives no precipitate or only a very slight transparent flocculency.

Picric acid (1 : 100) yields a fine lemon-yellow precipitate, in solutions stronger than 1 per cent., which is soluble in acids, but in dilute solutions yields no precipitate. Even in moderately strong solutions the precipitate formed by the first drop or two of reagent redissolves. The precipitate with α-eucaine is more insoluble than either of the others, and comes down accordingly, in somewhat more dilute solutions.

Iodine in alcohol yields a brown precipitate soluble in excess.

Fröhde's reagent (sulphomolybdic acid) gives no precipitate.

Mercuric chloride (1 : 20) gives no precipitate in dilute solution but in moderately strong solutions gives a fine white precipitate, easily soluble in excess.

Ferric chloride and potassium ferricyanide mixed give no precipitate except a white one in strong solutions. Allen[1] states that cocaine gives a precipitate of Prussian blue, but I have not been able to obtain it. Ferric chloride is stated by some authors to turn red on boiling one or two drops of a dilute solution with cocaine, owing to the formation of benzoate of iron. But as it also turns red with either of the eucaines or simply with distilled water the reaction is of no value. It gives no precipitate even in strong solution.

Cadmium iodide gives a white precipitate.

Potassium ferrocyanide gives in solution of about 10 per cent. a slight colorless gelatinous precipitate. A saturated solution of β-eucaine does not yield this precipitate probably because the solution is too weak.

Potassium ferricyanide gives a white precipitate in moderately strong solutions, which is more easily thrown down if solution is acid with hydrochloric acid.

Potassium bromide, chloride, or bromate give no reaction.

If a few drops of a solution of either of the hydrochlorides of α- or β-eucaine or cocaine be acidified with strong nitric acid, evaporated to dryness in a watch-glass, and treated with 1 or 2 drops of a solution of alcoholic potash, a very characteristic odor of benzoic ethyl ester is obtained. This reaction would probably also be given with other alkaloids containing the benzoyl group.

[1] "Commercial Organic Analysis," Vol. III, part II, p. 275.

REACTIONS CHARACTERISTIC OF α-EUCAINE SALTS.

Potassium iodide (1 : 10) gives, in even moderately dilute solutions of α-eucaine hydrochloride, a white silky and glistening precipitate. This precipitate has much the same appearance as the one obtained when stannous chloride is added to a cold dilute solution of mercuric chloride. β-Eucaine and cocaine give no reaction.

Ammonia, even in dilute solution, precipitates the bases α- or β-eucaine or cocaine, but α-eucaine is almost insoluble in excess. In 1 per cent. solution the white precipitate is at once thrown down, and in the case of β-eucaine or cocaine dissolves immediately on addition of about their own volume of strong ammonia. α-Eucaine, so precipitated, can be diluted at least ten times with strong ammonia without solution. In stronger solutions the difference still exists but is not so easily recognized. A 3 per cent. solution of β-eucaine or cocaine requires about five times its own volume of ammonia to be dissolved and stronger solutions much in proportion to the per cent. present. In other words a strong solution of ammonia will dissolve about one-half of one per cent. of the bases β-eucaine or cocaine, while it will dissolve but a very small fraction of a per cent. of α-eucaine. In dilute solutions this is a very characteristic reaction for α-eucaine and strong solutions are, of course, very easily rendered dilute for the test.

Potassium dichromate, in strong solution, added drop by drop to a 0.5 to 1 per cent. solution of α-eucaine, begins to throw down a fine lemon-yellow precipitate after addition of 1 or 2 drops. The precipitate is then much increased by 1 or 2 drops of strong hydrochloric acid, and is then quite insoluble, dissolving only after several times diluting the volume of the solution. With stronger solutions the precipitation takes place at once, the first drop giving a more and more permanent precipitate as the solution grows stronger. The precipitate is notably insoluble in either water or hydrochloric acid. More dilute solutions either show no precipitate or only after addition of hydrochloric acid. Cocaine, 1 per cent. solution, is not precipitated by potassium dichromate, but the addition of 1 or 2 drops of concentrated hydrochloric acid throws down a yellow precipitate easily soluble in very slight excess of hydrochloric acid or on dilution of the solution with water. Weaker solutions do not precipitate while stronger solu-

tions precipitate at once. The precipitate is, however, easily soluble as before. β-Eucaine acts like cocaine. The precipitate in all cases is lemon-yellow. The α-eucaine precipitate is quite crystalline. All three may throw down a small amount of a yellow colloidal precipitate which sticks to the side of the test-tube and dissolves but slowly, although this in no wise interferes with the test and does not take place if reagents are added slowly. While this test depends upon the very much greater insolubility of the α-eucaine salt, the non-precipitation in dilute solutions of a certain strength until after the addition of hydrochloric acid is quite characteristic for all. The correct strength is about 0.5 per cent. solution of α-eucaine and about 1 per cent. for β-eucaine and cocaine. In the case of cocaine and β-eucaine, the test may be conveniently applied by precipitating a stronger solution than 1 per cent. with potassium dichromate solution, diluting carefully with water until precipitate just dissolves. On addition of a drop of concentrated hydrochloric acid the precipitate will at once re-form. This can not be done with α-eucaine for precipitate once formed it is difficult to get it to dissolve at all.

Chromic acid (1 : 20) acts similarly to the dichromate.

REACTIONS OF COCAINE DISTINGUISHING IT FROM EITHER α- OR β-EUCAINE OR FROM BOTH.

If a small amount of cocaine hydrochloride be rubbed up with dry mercurous chloride (calomel), and then moistened with alcohol, it rapidly turns to a grayish black. α-Eucaine hydrochloride becomes slowly a dark gray. β-Eucaine hydrochloride is not affected.

Platinic chloride throws down slowly a yellow crystalline precipitate from a 1 per cent. solution of cocaine hydrochloride which is insoluble in hydrochloric acid. α- and β-eucaine hydrochloride in 1 per cent. solution are not altered. In stronger solutions all three hydrochlorides are immediately precipitated by platinic chloride but the cocaine precipitate is not soluble in hydrochloric acid while the precipitates by either eucaine are at once dissolved.

F. Giezel[1] has pointed out that the permanganate of cocaine is much more stable than that formed by most other alkaloids. This fact gives rise to one of its most distinguishing reactions.

[1] *Pharm. Ztg.*, p. 132 (1886).

The test is best applied upon a microscopic slide or in a small watch-glass. A drop of a solution of the hydrochloride is placed upon the glass and a very small drop of a solution of potassium permanganate is added. If the solution is strong enough for a precipitate to appear at once the change can be observed on the precipitate but it is preferable to watch the change of color of the solution itself. With either of the eucaines the color almost immediately begins to change to brown while with pure cocaine the original color holds generally for fully half an hour but also eventually changes to brown. The cocaine precipitate examined under the microscope is a beautiful violet-red which also in time turns to brown. This is true of the eucaine precipitates at first but they rapidly change to brown. Excess of permanganate should be avoided.

Cocaine hydrochloride in solution in either water or alcohol polarizes light strongly to the left. Antrich[1] states that this is the best test for the purity of the salt. According to this authority for aqueous solution $S_d = -52.2$ and for solution in alcohol of 0.9355 sp. gr., $S_d = -68.06$. A solution of the hydrochlorides of either α- or β-eucaine does not polarize light.

Cocaine when used in the eye almost always causes mydriasis. β-Eucaine does not dilate the pupil.

REACTIONS CHARACTERISTIC OF β-EUCAINE HYDROCHLORIDE.

The chief characteristic property of β-eucaine hydrochloride is its comparative insolubility in water and alcohol and it is readily distinguished from cocaine by this property. A small test sample of cocaine hydrochloride, if moistened with its own volume of alcohol or water, dissolves at once, while β-eucaine hydrochloride is little affected. In making the test, however, where weighed quantities are not used it should be remembered that even β-eucaine is soluble to the extent of 11 per cent. in alcohol and a too large amount of the solvent should not be used. Just enough to moisten is all that is necessary to dissolve cocaine or α-eucaine hydrochloride.

No chemical reactions of a positive character have been found characteristic of β-eucaine, but the results with permanganate, mercurous chloride, platinic chloride, and polarized light, will identify cocaine, while the tests with potassium iodide, potassium

[1] *Ber. d. chem. Ges.*, **20**, 310.

chromate and ammonia will distinguish it from α-eucaine. These with the other reactions noted will serve to separate it from other alkaloids.

MICROSCOPIC CHARACTERISTICS.

A careful examination of many of the precipitates which the various reagents yield with either of the eucaines or with cocaine failed to disclose any special characteristic of value. Many of them are beautifully crystalline and give striking displays of color with polarized light, but they vary too much with different conditions to be used with certainty as a means of identification. An examination of the alkaloids themselves as precipitated by ammonia and crystallized from chloroform also give negative results. Fortunately, however, the hydrochlorides, when pure, are easily identified under the polarizing microscope and especially is cocaine hydrochloride recognizable at once.

The slides are best prepared by allowing a drop of an aqueous solution to spontaneously evaporate. Cocaine under these conditions does not always crystallize at once even when quite dry. But if set aside for a few hours the crystals will form and the peculiar feathery and fan-shaped radiations, resembling very closely those seen on a broken nodule of wavellite, are recognizable even with the naked eye. The examination is most satisfactorily performed with a magnifying power of about 250 diameters.

α-Eucaine hydrochloride in saturated solution tends to crystallize in little spots which, under polarized light, look like very highly colored rosettes made up of very small crystals, so that the field is always bright, never showing any constancy of extinction directions. On edges of drop, the rosettes sometimes show small feathery forms of crystals of which the extinction directions vary but are more often diagonal. A 5 per cent. solution gives much the same result. The rosettes frequently appear to be made up of concentric rings of very small crystals, the center of rosettes being thicker than edges and only the edges showing plate or feather forms large enough to be examined as individuals. Interference colors are very bright. When crystallized from dilute solution the rosette forms may become very small and numerous, covering the entire field while the interference colors are only gray or black. The forms of gray and black overlying feathers

are at times very prominent in α-eucaine and resemble nothing so closely as the small feathers of Plymouth Rock poultry.

β-Eucaine hydrochloride from saturated solution shows broad feathery or fern-like forms, sometimes blade-like or tabular. Usually the tabular forms show concentric rings of high color around the edges and the extinction directions are easily determined. They are usually slightly oblique to the main axis of the crystal, but different crystals show two separate angles of extinction, one being the complement of the other and due to the fact that the individuals are viewed from opposite sides. The forms already mentioned are more apt to be found around the outer edge of the evaporated drop while the center is made up of isolated individuals which show brilliant tabular and prismatic forms sometimes quite small and rod-like. Rarely they are diamond-shaped. These diamond-shaped forms sometimes show extinction directions symmetrical to the main axis, but more often slightly oblique. The individual crystals are large and much more easily studied than those of α-eucaine. If more dilute solutions of less than 1.5 per cent. are used, the characteristics do not come out so plainly, the crystal forms being smaller and showing very low interference colors, mainly light grays. Also these sometimes show feathery forms and rosette forms something like α-eucaine.

Cocaine hydrochloride in 10 per cent. to 1 per cent. solution crystallizes in fan-like shapes. A 2 per cent. solution gives a solid field of radiating forms, the individuals of which resemble very closely the forms sometimes seen on a frosted window. Extinction is parallel and perpendicular to the main axis of the crystals. Colors are brilliant and the whole field is characteristic, enabling one to distinguish cocaine immediately. With dilute solutions the fan-like shapes are still marked, but the field is sometimes broken and interference colors are a low order of light grays.

In conclusion it is perhaps well to suggest that in working on unknown substances all tests for eucaine and cocaine, as with other alkaloids, are much more valuable when compared with those of samples whose identity is known.

NEW HAMPSHIRE COLLEGE.

SOME HYDROCHLORATED SULPHATES.

By Charles Baskerville.

Received August 16, 1901.

SMITH and Tunnell[1] have published experiments on the removal of the acid radical in sodium and potassium sulphates by gaseous hydrochloric acid under the influence of heat. The volatilization, rather substitution, of sulphuric acid by hydrochloric acid has been pointed out in papers presented before the North Carolina Section by the writer. Heusgen[2] had previously noted that gaseous hydrochloric acid acted upon potassium sulphate cold. Prescott[3] observed substitution when the same salt and concentrated hydrochloric acid were evaporated together. Smith obtained addition products, *i. e.*, $K_2SO_4.xHCl$ (x not stated), in the course of the reaction, but a complete elimination of the sulphuric acid was not observed. The reaction is attributed to mass action.

Our observations on somewhat similar reactions were made with salts of zinc, cadmium, and mercury. The experiments demonstrate without doubt the effect of mass action, but time, temperature, and the removal from the sphere of action of certain agents involved have a decided influence on the observed changes.

The degree of substitution depends entirely upon the temperature and time of the action as well as mass. The preparation of new bodies like these is of no great importance. The point of interest rests in the graduated substitution of water by hydrochloric acid, molecule for molecule, in crystalline bodies. This substitution may throw some light upon the discussed "molecular compounds."

MERCURIC COMPOUNDS.

(With Lionel Weil.)

According to Berzelius, if a stream of hydrochloric acid gas be passed over mercuric sulphate, mercuric chloride and sulphuric acid will result. Ditte[4] states that if gentle heat be applied, the mercuric sulphate combines with hydrochloric acid, melts and snow-white crystals of $HgSO_4.HCl$ are sublimed. Further the same compound may be obtained by evaporating mercuric sulphate and concentrated hydrochloric acid, or mercuric chloride and

[1] This Journal, **21**, 930 (1899).
[2] *Ber. d. chem. Ges.*, p. 1671 (1876).
[3] *Chem. News*, **36**, 178.
[4] *Ber. d. chem. Ges.*, **12**, 361 (1879).

sulphuric acid with 1 molecule of water. By gentle heat, white needle crystals are obtained.

The experiments were repeated successfully in the following way: Twenty grams mercuric sulphate were treated with 20 cc. concentrated hydrochloric acid in a porcelain dish, the excess of acid being first driven off by a free flame; the substance was dried on a sand-bath and sublimed at 240° C. into a funnel, through which a rapid stream of air was drawn. The crystalline sublimate was treated in turn with alcohol and a mixture of alcohol and ether to remove the free acid and mercuric chloride and sulphate. The insoluble portion was not affected by hydrochloric acid and was only slightly soluble in nitric acid. It was fused with sodium carbonate, leached, and the chlorine determined.

	Calculated for $HgSO_4.HCl$.	Found.
Chlorine	10.67	10.81

The yield was small and not improved by varying the amounts of the substances used.

In following out another method for preparing hydrochlorated mercuric sulphate, namely, by gently heating the mercuric sulphate in a stream of dry hydrochloric acid, only a small amount of the substance was obtained. A new white, crystalline, very deliquescent body was obtained however which proved on analysis to be the dihydrochlorated body, which is very soluble in water.

	Calculated for $HgSO_4.2HCl$.	Found.
Sulphur trioxide	18.65	18.18

Roscoe and Schlorlemmer state that mercuric chloride dissolves without decomposition in concentrated sulphuric acid. This seems to be true, but, on heating, a crystalline sublimate was obtained in the funnel suspended above the dish in which the reaction occurred. If the heating be too prolonged some free sulphuric acid will volatilize and condense on the crystals. Molecular amounts of mercuric chloride and $H_2SO_4.H_2O$ were carefully heated in a porcelain dish. Clean, dry, well-formed monoclinic crystals were selected from the sublimate in the neck of the funnel suspended above. On analysis these crystals gave the following results:

	Calculated for $HgSO_4.2HCl.H_2O$.	Found.
Chlorine	18.34	19.89

The substance was not further worked with.

CADMIUM COMPOUNDS.

(WITH ISAAC F. HARRIS.)

By varying the temperatures we have succeeded in replacing variable amounts of water of crystallization in $3CdSO_4.8H_2O$. At 150° C. the sulphate loses 4 molecules of water; if subjected to the action of dry hydrochloric acid at that temperature 4 molecules of hydrochloric acid combine with the partially dehydrated body, giving $3CdSO_4.4H_2O.4HCl$.

At 200° C. the hydrated sulphate permits all its water to be expelled, giving $3CdSO_4.8HCl$. At that temperature under the prolonged influence of the hydrochloric acid, or at dull red heat for a shorter period, the sulphuric acid radical is displaced and finally $CdCl_2$ results. The observations noted took place with the hydrated sulphate, or material dried at 150° C. or completely dehydrated.

The bodies obtained are very deliquescent and present difficulties in obtaining them pure for analysis. Hydrochloric acid is held mechanically by the compounds and is difficult to remove. The method of procedure was to place the sulphates, hydrated and anhydrous, in a porcelain boat in combustion tubing fixed in an air-bath punctured to admit the tube. Dry hydrochloric acid was passed through the tube whose temperature was closely guarded. The material melted and crystallized out on cooling. If the temperature reached dull redness (with experiments over direct flame) the body was sublimed to the cooler portions of the tube. In order to remove the mechanically bound hydrochloric acid, the tube was allowed to cool for twelve hours, a steady stream of gas passing through all the while; afterwards dry air, free from carbon dioxide, was passed through for two or more hours. Some analyses are appended.

		Calculated.	Found. I.	Found. II.
Original sulphate $3CdSO_4.8.H_2O$	SO_3	31.2	31.4	
	H_2O	18.7	18.1	
$3CdSO_4.4H_2O.4HCl$ (at 150° C.)	HCl	17.00	16.00	18.7
			16.00	
	SO_3	28.00	28.00	27.5
With prolonged heating	HCl		22.5	
	SO_3		23.5	
Fused and partially volatilized $3CdSO_4.8HCl$	HCl	31.00	30.1	30.2
Continued heat and sublimation $CdCl_2$	Cl	38.6	38.00	

A few experiments were made with zinc sulphate and the above observations extended, but not completed.

UNIVERSITY OF NORTH CAROLINA,
April 23, 1901.

THE ACTION OF ZINC ETHYL UPON NITRO AND NITROSO COMPOUNDS.

(A REPLY TO I. BEWAD.)

BY ARTHUR LACHMAN.

Received September 28, 1901.

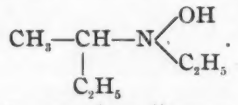
IN a recent paper containing a wealth of experimental material, I. Bewad undertakes to prove the complete analogy of the action of zinc ethyl on carbonyl compounds on the one hand, and upon nitrogen-oxygen compounds on the other. This work was begun about fourteen years ago,[1] but its most important results were not manifest, or at any rate were not published in accessible journals, until last year.[2] In his last paper Bewad is anxious to claim priority for these results, evidently with reference to my own publications,[3] since the general subject has not been investigated by any third party.

Bewad's priority in this work is unquestioned. In fact, it was through a study of Bewad's own publications that I was led to attempt the main problem I have undertaken; *viz.*, the intimate structure of the nitro group. Priority, however, is no guarantee of accuracy; and since Beward has been, and is still, in error as to some matters of fact, and is entirely at sea with his explanations of other facts, I have thought it desirable to clear up several points that would seem reasonably certain, before proceeding with new experimental work.

In order to indicate that Bewad's results in the past have needed revision, let me briefly append a history of events. In his first papers (*cf.* above), Bewad asserted the following: That the action of zinc ethyl on nitroethane gave triethylamine oxide, $(C_2H_5)_3N=O$; that the reaction succeeds with only one molecule of zinc ethyl; that if two are taken, no amine oxide at all is obtained; that upon reduction the amine oxide forms triethylamine. On the other hand, I showed in my first paper that if two molecules of zinc ethyl are taken the yield of "amine oxide,"

[1] *Cf. Ber. d. chem. Ges.*, **21**, ref. 479 (1887); **22**, ref. 250 (1888).
[2] *J. prakt. Chem.*, **63**, 94 (1901).
[3] *Am. Chem. J.*, **21**, 433 (1899); *Ber. d. chem. Ges.*, **33**, 1022 (1900).

instead of vanishing, is more than doubled (a discovery which Bewad seems to have made for himself subsequently). But what is most important is that no amine oxide whatever is formed, but instead ethyl-sec. butylhydroxylamine,



Bewad was fortunate enough to discover this for himself. The previously noted reduction to triethylamine was erroneous.

My own work on the nitro group took its start from the then unquestioned existence and method of formation of triethylamine oxide. All of the conclusions contained in my first publication are therefore futile, and are herewith withdrawn.[1] To be sure, the real triethylamine oxide has subsequently been found by Dunstan and Goulding,[2] and by myself,[3] but its method of formation does not bring it into connection with the nitro group.

It is to Bewad's explanation of the mechanism of his results, however, that I wish to call attention. To begin with the facts first, Bewad has found that when alphyl nitrites are treated with zinc ethyl and then with water, the products are alcohols and diethyl hydroxylamine (and of course zinc hydroxide); *e. g.*,

$$[C_3H_7O.NO + Zn(C_2H_5)_2] + 2H_2O =$$
$$C_3H_7OH + (C_2H_5)_2NOH + Zn(OH)_2. \quad (I)$$

On the other hand, I have found that when diphenylnitrosamine is treated with zinc ethyl, the products are diphenylamine and diethylhydroxylamine:

$$[(C_6H_5)_2N.NO + Zn(C_2H_5)_2] + 2H_2O =$$
$$(C_6H_5)_2NH + (C_2H_5)_2NOH + Zn(OH)_2. \quad (II)$$

If we designate, in these two equations, the group attached to —NO by X, the two reactions are exactly parallel:

$$[X—NO + Zn(C_2H_5)_2] + 2H_2O =$$
$$X—H + (C_2H_5)_2NOH + Zn(OH)_2. \quad (III)$$

It is a reasonable assumption that the mechanism of this reaction is identical in both cases.

In (II), I was able to show, by separating and analyzing the first product, that one molecule each of nitrosamine and zinc ethyl

[1] *Am. Chem. J.*, **21**, 440 (1899).
[2] *J. Chem. Soc.*, **75**, 792 (1899).
[3] *Ber. d. chem. Ges.*, **33**, 1025 (1900).

unite to form a stable compound, which is subsequently decomposed by water:

$$(C_6H_5)_2N{-}NO + Zn(C_2H_5)_2 = (C_6H_5)_2N{-}N\begin{matrix}C_2H_5\\ \diagup\\ Zn\\ |\\ O\\ \diagdown\\ C_2H_5\end{matrix};$$

$$(C_6H_5)_2N{-}N\begin{matrix}C_2H_5\\ \diagup\\ Zn\\ |\\ O\\ \diagdown\\ C_2H_5\end{matrix} + 2H_2O =$$

$$(C_6H_5)_2NH + N\begin{matrix}C_2H_5\\ \diagup\\ -OH\\ \diagdown\\ C_2H_5\end{matrix} + Zn(OH)_2. \quad (IV)$$

The decomposition products agreed closely with the calculated yield (diphenylamine quantitative, hydroxylamine over 50 per cent.). Bewad, on the other hand, led by the analogy of the carbonyl group, —CO, assumed that two molecules of zinc ethyl would be required, did not try to use merely one, did not separate or analyze his addition product, and gives the following equation:

$$R{-}O{-}NO + 2Zn(C_2H_5)_2 =$$

$$R{-}O{-}N\begin{matrix}O{-}Zn{-}C_2H_5\ (B)\\ \diagup\\ Zn{-}C_2H_5\\ \diagdown\\ C_2H_5\\ C_2H_5\end{matrix} (+ 4H_2O) =$$

$$R{-}OH + (C_2H_5)_2NOH + Zn(OH)_2 + [Zn(OH)_2 + 2C_2H_6]. \quad (V)$$
$$(B)$$

I have labeled the two zinc ethyl molecules in order to point out that molecule (B) simply adds on to the first product, and then splits off again, for no other apparent purpose than to gratify Bewad's sense of analogy.

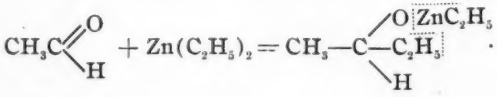
From the above it would appear that we have a very general reaction of the nitroso group when not attached directly to carbon. In this latter case, I have found nitrosobenzene to behave altogether differently, for reasons that cannot yet be understood.[1]

One seeks in vain for any analogy between this general reaction of nitroso compounds and the behavior of carbonyl groups with zinc ethyl. Bewad compares the former to the reaction of alde-

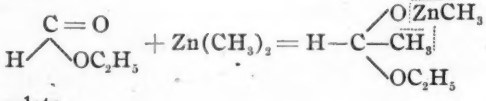
[1] *Cf. Am. Chem. J.*, **21**, 442 (1899).

hydes, formic and oxalic esters, etc.[1] But in all of these instances one molecule of zinc alphyl is able to introduce only one hydrocarbon radical.

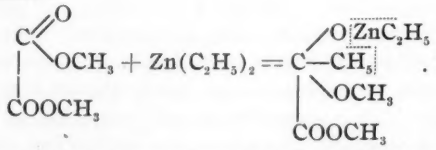
Aldehyde :



Ethyl formate :

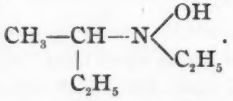


Methyl oxalate :



The behavior of the nitroso group is therefore unique, and in no way parallel to that of carbonyl.

The behavior of nitro compounds with zinc ethyl is much more complicated. As Bewad's equations are highly complex, as he is guided wholly by the misleading carbonyl analogy, and as some of his formulas are self-contradictory, it is not necessary to devote further time to this side of his work. The facts are more important for the present. Bewad finds that zinc ethyl and nitroethane react slowly. If the mixture is decomposed after a few days, the main products are unchanged nitroethane and secondary nitrobutane. If allowed to stand several months, the nitro-paraffins diminish in amount, and the main product is then ethyl sec. butyl hydroxylamine :



An entirely similar reaction was obtained with numerous other nitroparaffins and zinc alphyls, provided that primary or secondary nitroparaffins are taken. (Zinc methyl with nitromethane forms an exception.)

[1] *Loc. cit.*, p. 110.

It is not worth while to supplement Bewad's speculations by others equally unfounded; but the following facts seem to stand out plainly. First, that the primary action of zinc alphyl is to alkylate, and that this alkylation is independent of the subsequent alteration of the nitro group; proof: nitrobutane is formed before the hydroxylamine. Second, that the new nitroparaffine thus formed is not present in the free state, but probably in the shape of a zinc alphyl salt; proof: if a primary nitro compound is the original substance, the resulting hydroxylamine contains a secondary radical; whereas if we start from a secondary nitroparaffin, we get a tertiary radical in the hydroxylamine. If free secondary nitroparaffins are first formed, we should obtain tertiary radicals in both instances. Third, that this intermediate product is capable of adding on zinc alphyl in such a way that one hydrocarbon radical attaches itself to nitrogen. This addition depends upon the previous compound, and is not wholly due to the nitro group.

The last conclusion needs further details. Bewad, in an experiment to which he himself attached but little importance, found that a tertiary nitroparaffine was simply reduced to the corresponding hydroxylamine without alkylation,

$$(CH_3)_3C{-}NO_2 \rightarrow (CH_3)_3C{-}N\begin{matrix}H\\OH\end{matrix};$$

the absence of a mobile hydrogen atom, with its consequent replacement by zinc alphyl, seems to prevent alkylation of the nitrogen atom.

On the other hand, we may have here a specific reaction of the nitro and the nitroso group when directly attached to carbon. The main product when nitrosobenzene acts upon zinc ethyl is phenylhydroxylamine.[1] Nitrobenzene also gives a small amount of phenylhydroxylamine.[2] Bewad found only aniline in this last case, but that is an error in fact; besides phenylhydroxylamine, I was able to isolate small amounts of aniline and ethyl aniline. Here again it will be best to refrain from speculative equations until further facts are obtained.

It is clear, however, that in the action of zinc ethyl on nitrogen oxygen compounds we have a process that is by no means analogous to the behavior of carbonyl compounds; that different

[1] Lachman: *Am. Chem. J.*, **21**, 343 (1899).
[2] *Ibid.*

classes of these nitrogen oxygen compounds behave altogether differently; and that only for the very limited group of nitroso compounds whose nitrogen atom is not directly linked to carbon is there anything like a clear comprehension of the details of the reaction.

EUGENE, OREGON,
August, 1901.

REVIEW.

A REVIEW OF SOME RECENT PROGRESS IN ORGANIC CHEMISTRY.[1]

It is with deep regret that I am obliged, at this first attempt of the Section, to bring a systematic review of recent progress in chemistry, to ask your kind indulgence for the many omissions and defects in this summary of the recent history of organic chemistry. The time at my disposal has been very short; the subject-matter, I need not say, is all too extensive. A painstaking German statistician has calculated that over 10,000 pages are needed to record the annual progress of organic chemistry. I have endeavored to report upon the work of some three years; the printed pages, if laid side by side, would make a solid field of type covering some 6,000 square feet—a large area for a critic to weed over by lamplight. Under the circumstances, I have ventured to select a few of what have seemed to me the more important achievements, and have called this paper "A Review of *Some* Recent Progress."

NOMENCLATURE AND REGISTRATION.

The important problem of naming organic compounds has not advanced much beyond the work of the Geneva conference in 1893. It will be remembered that the Geneva rules are fairly satisfactory only for the simpler fatty compounds; they are too cumbersome for complex fatty derivatives, and fail almost completely with the vast majority of ring compounds. It is still possible for ten chemists to describe one and the same substance under ten different names, without recognizing the identity of their descriptions. An important discovery by M. M. Richter, however, promises to be of great assistance in simplifying this difficulty. Richter has pointed out that while the name of an organic compound may not be characteristic, *its empirical composition is absolutely definite.* He has, therefore, undertaken the truly Herculean task of gathering nearly 80,000 organic substances together into a dictionary, grouping these according to the increasing complexity of their atomic composition. The result is a

[1] Read at the Denver meeting of the Society, August, 1901.

monumental work,[1] whose use enables the chemist to identify an unknown compound in the shortest possible time.

At first sight, it may appear that the Richter system has serious disadvantages. For instance, no less than 52 compounds of the formula $C_{12}H_{16}O_3$ are to be found in this dictionary. Even if we should ascertain this formula for a newly-found substance, a huge problem remains. On the other hand, it is to be observed first, that Richter is not responsible for the isomerism of these 52 compounds; and second, that by thus grouping them all together in one place, the comparison of data is greatly facilitated. As a matter of fact, the most superficial determination of properties, once the composition is known, is all that is needed to pick out the desired name from the list. The ability of the Richter system to stand the test of actual use is shown by its adoption for the index of several important journals; *e. g.*, the *Berichte*, the *Annalen*, and the *American Chemical Journal*.

This general use of Richter's system is interesting from two rather different points of view. For one, it will serve to increase the respect of the organic chemist for quantitative analytical work. He has been compelled to identify his substances largely by their general reactions and relationships. He has even been proud of his skill in dispensing with analysis. But the analytical route is now the shortest method of identifying substances, and the organic chemist must again be broiled over his combustion furnace as in Liebig's time. I venture to predict a speedy improvement of this venerable contrivance.

The second feature takes a speculative turn. The present development of organic chemistry is due to the discovery of isomerism; *i. e.*, of the fact that *empirical composition does not suffice* to characterize a substance. It is curious that the fruits of this discovery should bring us back to one of the earliest ideals of modern chemistry. How this would have pleased Berzelius!

In the way of special propositions in nomenclature, it is worth while to note the suggestions of Vorländer,[2] that *all* univalent hydrocarbon radicals, both fatty and aromatic, be designated by the old term *alkyl;* that fatty alkyls be called *alphyls*, and aromatic alkyls be named *aryls*. Mixed fatty and aromatic radicals, such as benzyl, are to be called *alpharyl*. Acid radicals are to have the class name *aryl*, from which are then derived *alphacyl* and *aracyl* for fatty and for aromatic acid radicals, respectively. These suggestions seem to have been widely adopted.

The need of some comprehensive method of naming and registering organic compounds has been shown by Rey and by Kaufman,[3] in rather alarming fashion. Assuming not more than nine different substituents, hydrogen included, in the naphthalene

[1] "Lexikon der Kohlenstoffverbindungen."

[2] *J. prakt. Chem.*, **59**, 247 (1899).

[3] *Ber. d. chem. Ges.*, **33**, 1910, 2131 (1900).

nucleus, 10,766,601 derivatives are possible. Organic chemistry is not likely to perish for lack of material, it would appear.

We cannot do more than refer here to Baeyer's proposed nomenclature for the so-called condensed carbon rings.[1] As with all of Baeyer's proposals, this one is sure to be universally employed.

MISCELLANEOUS COMPOUNDS AND REACTIONS.

Under this heading will be given a number of interesting or important facts that cannot well be classified under other topics. The order of arrangement is merely one of convenience.

The *paraffin hydrocarbons* will soon no longer deserve their name. The difference between them and the aromatic hydrocarbons, once so marked, has been shown by Worstall to be only a matter of degree.[2] They are attacked both by concentrated nitric and sulphuric acids, yielding nitroparaffins and sulphonic acids, just as benzene does. The action is much slower than in the latter case, however, and seems to reach its equilibrium at a much lower percentage of transformation.

In the *sugar group*, Ruff[3] has discovered a new method of passing from one sugar to the next lower in the series. This method consists in the oxidation of the calcium salts of the corresponding acids with hydrogen peroxide. He was thus able to prepare *d*-erythrose from *d*-arabinose, and to establish the generic relationship of the former to the sugar series.

Graphitic acid, obtained by the oxidation of graphite, has long been regarded as one of the mysteries of chemistry. It has recently been investigated by Staudenmaier,[4] who concludes that it is likely to remain a mystery for some time to come. The formulas and properties that have been previously ascribed to its various derivatives are entirely unreliable. Staudenmaier has found a very easy method of preparing the acid, suitable for lecture demonstration.

It will be remembered that a few years ago Nef was able to bring to a conclusion a century's work on *fulminic acid*, by showing that this interesting acid is the oxime of carbon monoxide, C=N—OH. This has recently been substantiated in a curious manner by Scholl.[5] The Friedel-Crafts reaction of mercury fulminate, benzene and aluminum chloride leads to the synthesis of benzaldoxime:

$$C_6H_6 + C{=}N{-}OH = C_6H_5CH{=}N{-}OH.$$

The Friedel-Crafts reaction itself, which Baeyer has called the magic trunk of the wizard because of the wonderful things it

[1] *Ber. d. chem. Ges.*, **33**, 3771 (1900).
[2] *Am. Chem. J.*, **21**, 210 (1899); **20**, 664 (1898).
[3] *Ber. d. chem. Ges.*, **32**, 3672 (1899).
[4] *Ibid.*, **32**, 2824 (1899).
[5] *Ibid*, **32**, 3494 (1899).

furnishes in inexhaustible supply, has been the object of careful study by Perrier[1] and others; and before long we may hope to understand this important process to a degree befitting its importance.

The bitter struggle over the constitution of the *diazo compounds* is drawing to a close. It will be remembered that Hantzsch has contended for a stereochemical explanation of diazo isomerism, whereas Bamberger stood out for a structural explanation of these phenomena. It would take us too far afield to enter into the details of this controversy here, and a few observations must suffice. Bamberger for the last three years has been allowing his case to go by default, a sign that he has recognized his defeat. Quite recently he has made an important admission of error with reference to the metallic derivatives of the diazo compounds. Hantzsch, meanwhile, with the agility that has characterized the evolution of his views, has returned to the proposition he had so strenuously opposed at first, that the isodiazo compounds are true nitrosamines in the free state. In connection with the diazo compounds, Hantzsch has elaborated a new theory of chemical processes which will be considered below.

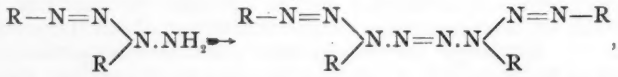
The *uric acid* group is witnessing a decided "boom" during the last few years. Fischer's syntheses in this group are too well known to refer to now. W. Traube has recently discovered an entirely new synthesis of uric acid and its numerous congeners.[2] The method is too complex for description here; suffice it to say that it starts with cyanacetic acid, a compound easy to obtain in large quantities, and that Traube has already succeeded in obtaining xanthine, guanine, uric acid, and numerous alkylated derivatives of these. The yields are said to be almost quantitative.

The remarkable activity of investigation and synthesis in the uric acid group undoubtedly owes its origin to the hope of commercial success. Fischer's work has shown a very close connection between caffeine and uric acid; and a moderate fortune awaits him who will be able to prepare caffeine cheaply by a synthetic process. Aside from this material interest, however, the uric acid group occupies an important position in the purely scientific aspects of chemistry. On the one hand, the function of uric acid and its derivatives within the animal organism is a topic of the profoundest importance to physiology and dietetics. Great progress is to be expected when the advertisements of the Michigan "health food" people will be published in befitting detail in the *Berichte*. And on the other hand, a very curious isomerism has been brought to light among the mono-methyl uric acids. Four of these are foreseen by structural theories, whereas Fischer and Ach[3] have already discovered six. No explanation is offered

[1] *Ber. d. chem. Ges.*, **33**, 815 (1900).
[2] *Ibid.*, **33**, 3035 (1900).
[3] *Ibid.*, **32**, 2723 (1899).

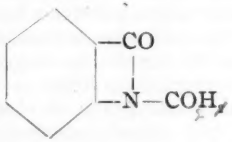
so far, except that Fischer, than whom no man is a better judge, has expressed his conviction that stereochemistry and tautomerism have no application here.

Among the large number of curious *nitrogen compounds and reactions* discovered during the past few years, a few must answer for the present. A long chain of nitrogen atoms has been prepared by Wohl and Schiff.[1] By oxidation of the so-called diazohydrazides,

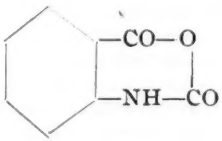


which contain four nitrogens in a chain, octazons with eight atoms are produced. The mere existence of these chains is an important contribution to our knowledge of the combining power of nitrogen.

Another interesting datum with reference to this combining power is found in the structure of isatoic acid. Erdmann[2] has shown that this acid, which for a long time was supposed to have the formula I, really has the formula II:



I.

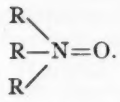


II.

The interesting feature of this discovery, which Erdmann seems to have missed, lies in the fact that until now isatoic acid was the only substance which had a free carboxyl group, —COOH, directly attached to nitrogen. Carbamic acid, H_2N—COOH, for example, is incapable of existing in the free state, and is known only in the shape of salts, esters, and other derivatives. It has now been shown that isatoic acid possesses a different structure than the one formerly assigned to it, so that we are forced to regard the combination of a carboxyl group with nitrogen as one of the incompatibilities of nature.

A third interesting discovery in the nitrogen territory was made independently by Wolffenstein, Bamberger, and Dunstan and Goulding. These investigators found that basic nitrogen atoms, as contained in the various amines, can be directly oxidized with hydrogen peroxide, yielding hydroxylamine derivatives. The most curious of these are the amine oxides, of the general formula

[1] *Ber. d. chem. Ges.*, **33**, 2741 (1900).
[2] *Ibid.*, **32**, 2159 (1899).



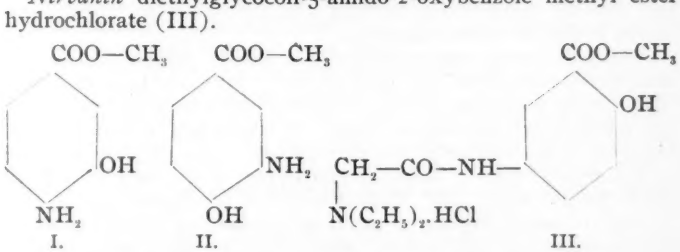
The amine oxides will play an important part in the future history of nitrogen.[1]

More or less connected with the chemistry of nitrogen, though in a manner by no means understood, are the *artificial medicaments*. It is a remarkable fact that very many of the most powerful drugs, including, of course, all the alkaloids, contain nitrogen. This is true of the artificial as well as of the natural members of the materia medica. I need only instance phenacetine and antipyrine. The study of the connection between chemical compositions and physiological action is steadily progressing, and the time seems not far distant when the scientific practitioner will invent new compounds off-hand at the bedside, instead of relying upon the pharmacopoeia. A long step in this direction has been taken by Einhorn,[2] who by systematic planning has obtained three new substitutes for cocaine :

Orthoform, *p*-amido-*m*-oxybenzoic methyl ester (I).

Orthoform new, *m*-amido-*p*-oxybenzoic methyl ester (II).

Nirvanin diethylglycocoll-5-amido-2-oxybenzoic methyl ester hydrochlorate (III).



I. II. III.

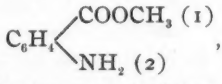
These anesthetics found immediate entrance into medical practice.

Attention should be called to a curious fact in all of the above formulae : *viz.*, that the *methyl* esters of the various substituted benzoic acids have been selected. The corresponding *ethyl* esters have no marked anesthetic properties. Here is a flagrant breach of the law of homology, which calls for protest from the systematists. It is a common statement in text-books of organic chemistry that all the members of a homologous series have identical chemical properties ; yet here we find the simple substitution of ethyl for methyl annihilating the most characteristic property of some rather complicated compounds. This remarkable influence

[1] *Cf.* Lachman : *Ber. d. chem. Ges.*, **33**, 1038 (1900).

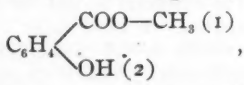
[2] *Ann. Chem.* (Liebig), **311**, 33 ff (1900).

of the methyl group is not confined to drugs. It has recently been found that the *methyl ester of anthranilic acid*,



is one of the essential odorous principles of the orange blossom and the jasmine.[1] The corresponding *ethyl* anthranilate is almost odorless.

A similar instance is to be found in the esters of salicylic acid; methyl salicylate is the oil of wintergreen,



whereas ethyl salicylate has only a faint ethereal odor.

The above investigation of orange and jasmine oils furnished an additional surprise; for it transpired that the sweet, penetrating perfume of these flowers was due in no small part to *indol!!* Indol, a constant ingredient of feces, has long been noted for its penetrating qualities; its sweet perfume comes as a surprise to many a patient, long-suffering chemist. Yet there seems to be no doubt that pure indol has a decided perfume odor, and that the disagreeable smell of the substance as usually obtained is due to some impurities.

A friend of mine once advanced the theory that all pure substances were odorless, and that all odors were due to impurities. This theory was born of an article that harks back several years, but which is worth reviving here. It was found by Finckh[2] that the odor of the sulphides and mercaptans can be entirely removed by a simple process. Now the mercaptans have been known to cause public riots; and Emil Fischer once showed that 1/460,000,000 of one milligram of ethyl mercaptan can be detected by the average unaided human nose. Yet the pure mercaptan is odorless; so that this small amount of mercaptan that Fischer smelled owed its recognition to the much smaller amount of the impurity which it contained. An interesting corollary of my friend's theory is that even this impurity is odorless in the pure state, and owes its odor to the presence of some other impurity. The subject is a promising one for investigation.

The importance of *physical chemistry* for the development of organic chemistry is increasingly manifest, and grows day by day. I need not more than refer to the use of physical constants in the determination of molecular structure; the methods and results of "spectro-chemistry," molecular-volumetric studies, thermochemical investigations, etc., are sufficiently well known. It will be sufficient to emphasize the warning that all of these methods

[1] Hesse: *Ber. d. chem. Ges.*, **32**, 2611 (1899); H. and E. Erdmann: *Ibid.*, p. 1213.

[2] *Ber. d. chem. Ges.*, **27**, 1239 (1894).

depend upon extrapolations the moment they are applied to new classes of compounds, and that they share with all other extrapolations the risk of running ahead of the facts. This seems notably true of the spectro-chemical studies of nitrogen compounds. Nor need I refer to the use of electrolytic conductivity for studying the dissociation of organic acids, bases and salts; these applications are sufficiently obvious.

It is in the use of the physico-chemical methods of thinking that organic chemistry will make the greatest progress. Thus, the study of reaction velocities, of the really active molecules when two or more substances are brought together, of the consequences rather than of the fact of ionization, have already made notable additions to our comprehension of organic reactions. A few examples will suffice.

Thus, Lewkowitsch was able to show by a study of reaction velocities that when fats are saponified the acid radicals attached to glycerine are separated one at a time, and not all three simultaneously.[1] Hantzsch has made continual use of electrolytic methods for tracing out the isomerization of diazo compounds (the references are too numerous to be cited). Walker has shown that the historical isomerization of ammonium cyanate to urea takes place between the ions of the salt, and is not a so-called "molecular rearrangement."[2] And numerous investigations of organic reactions have been carried out by H. Goldschmidt and his pupils upon a physico-chemical basis.[3]

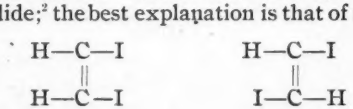
The use of the electric current for oxidizing and reducing organic compounds affords another instance of the interrelation of physical and organic chemistry. The successful employment of the electric current calls for a very careful study of the electrical processes themselves, as may be seen from the recent work of Tafel.[4] Once the details are mastered, however, excellent results can be obtained.

It is to be hoped that the time is not far distant when the word "catalysis" will vanish from the chemist's daily vocabulary. At present, it is merely a mystifying cloak to conceal our ignorance. It will be shown below that in the case of auto-oxidation the function of the catalyzer is growing clearer. Meanwhile, the discovery of new catalyzers, that is to say, of deeper mysteries of reaction, proceeds with unabated vigor. Michael has recently made the remarkable observation that the presence of methyl cyanide greatly increases the reaction-velocity of metallic sodium on organic compounds.[5] Thus, methyl iodide reacts very slowly with sodium in the cold; a few drops of methyl cyanide cause the reaction to proceed almost with violence.

[1] *Ber. d. chem. Ges.*, **33**, 89 (1900).
[2] *J. Chem. Soc.*, **71**, 489 (1897).
[3] *Cf. Ber. d. chem. Ges.*, **33**, 1140 (1900).
[4] *Ber. d. chem. Ges.*, **33**, 2209 (1900).
[5] *Am. Chem. J.*, **25**, 419 (1901).

The stereochemistry of carbon has made no notable progress during the last few years. A great deal of work has been done, but this has been devoted to extending our knowledge of the applications of stereochemistry rather than to enlarging our knowledge of the subject itself. In this connection, a recent utterance of Emil Fischer is of some significance.[1] He rebukes the general tendency to rush to stereochemistry as a final explanation of isomerism, and warns us to be ever mindful of its limitations and imperfections.

It is often the simplest cases of isomerism that are the hardest to explain. A simple case that *can* be explained therefore possesses a double interest. Keiser has obtained a second form of acetylene diiodide;[2] the best explanation is that of stereoisomerism:



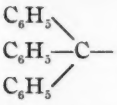
We are here crowding closely upon the final explanation of the isomerism of unsaturated compounds, for the geometrical interpretation does not please everybody.[3]

Another observation connected with stereochemistry deserves a moment's attention. W. A. Noyes has announced that optical activity may be present in substances that do *not* contain an asymmetric carbon atom.[4] Baeyer made a similar announcement a few years ago, and anent a very similar compound. Baeyer withdrew his announcement a few months later; I fear the similarity will extend to the same point in the former instance. Noyes' observation is important—if true.

Buchner's discovery that alcoholic fermentation is a chemical and not a physiological process is too well known to require detailed presentation here. Suffice it to say that the numerous skeptics who assailed this discovery at its first appearance, have either been silenced or convinced. One recent interesting confirmation is worth nothing; it is possible to kill the yeast cells completely, so that further growth and reproduction ceases; these dead yeast cells still possess the power of fermentation.[5] Further proof of non-vital fermentation would seem to be unnecessary; the fact being established, the mechanism now calls for careful study.

An observation that promises to be of much significance was recently made by Gomberg.[6] If triphenylchlormethane be treated with various metals, the halogen atom is removed, and a highly unsaturated hydrocarbon remains:

[1] *Ber. d. chem. Ges.*, **32**, 2726 (1899).
[2] *Am. Chem. J.*, **21**, 261 (1899).
[3] *Cf.* Micheal: *J. prakt. Chem.*, (2), **52**, 289 (1895).
[4] *Am. Chem. J.*, **24**, 289 (1900).
[5] *Cf.* Bokorny: *Chem. Centrbl.*, (1901), 1, p. 1207.
[6] *Cf. Am. Chem. J.*, **25**, 315 (1901).



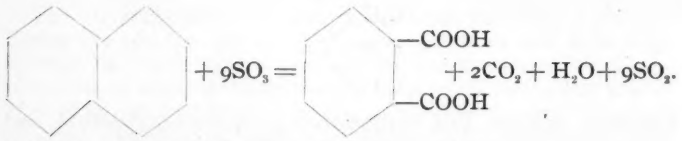
Gomberg assumes this hydrocarbon to be triphenylmethyl, and ascribes its unsaturated properties to the presence of a trivalent carbon atom. It is too early to dilate upon the consequences of this discovery; but when the conditions which limit the existence of trivalent carbon are better known, a rather serious review of present conceptions will be inevitable.

The chemistry of naturally occurring substances, which engrosses the attention of a large number of the world's most skilful chemists, is of rather too detailed and complicated a character to be incorporated in a brief review like this. To be properly presented, the progress made in the study of the terpenes, of camphor, of caoutchouc, of starch, of cellulose, of the innumerable natural and artificial dye-stuffs, should in each case have a whole paper devoted to that one subject only; and it seems better to omit their consideration altogether than to attempt a fragmentary and unsatisfactory jumble of facts.

The interests of the hour, however, permit of one exception to this sweeping exclusion. The chemical world has recently been stirred to the highest enthusiasm by the successful commercial synthesis of indigo. The laboratory synthesis of indigo was achieved long ago by Baeyer and others; but the transfer of this laboratory process to the factory on a scale to permit of competition with natural indigo offered innumerable obstacles, and over twenty years of unexampled industry and intelligence were necessary before the problem was solved. Many a sermon can be preached upon this achievement as a text; such as the examples set in patience, in foresight, in intelligent cooperation of the scientist and the technologist, in the expenditure of enormous sums for "scientific" work, etc. From the scientific side, it is a matter of chemical history that many of the modern problems and achievements took their rise in and around the investigations of indigo. H. Brunck, one of the directors of the "Badische Anilin und Soda Fabrik," has recently given an outline of the methods employed by his factory in the elaboration of their successful venture.[1] Permit me to outline the actual manufacture of indigo as it is carried out now by the Heumann process (D. R. P., 91202).

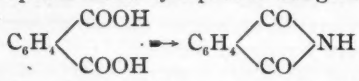
Starting with naphthalene, the cheapest and most abundant of the coal-tar ingredients, oxidation with highly concentrated sulphuric acid gives phthalic acid (and sulphur dioxide):

[1] *Ber. d. chem. Ges.*, **33**, Sonderheft, p. 71, (1900).

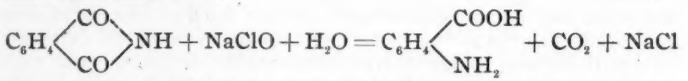


10,000 tons of naphthalene are used annually.

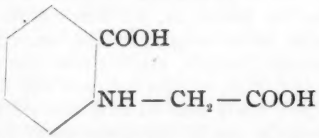
The recovery of this sulphur dioxide (some 40,000 tons annually) is an important matter; and it is interesting to note that the new "Badische" contact process is absolutely essential to the economical reconversion of sulphur dioxide into trioxide. This oxidation is accomplished by the air, so that at bottom it is the oxygen of the air that oxidizes naphthalene to phthalic acid. To give some idea of the immensity of this manufacture, even at this early stage of its development, a simple calculation shows that each year the oxygen standing over 1¼ acres of the earth's surface is completely exhausted. The phthalic acid thus obtained is converted into phthalimide by a process not given to the public:



Over 1,200,000 lbs. of ammonia are needed for the annual output. By means of sodium hypochlorite, phthalimide is converted into anthranilic acid:



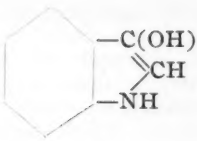
The anthranilic acid thus obtained is united with chloracetic acid, forming phenylglycocollorthocarboxylic acid:



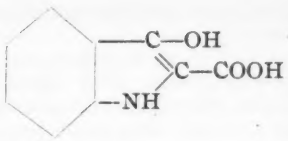
For this reaction, the "Badische" annually consumes 4,560,000 pounds of glacial acetic acid, requiring 26,000 cords of wood for their production. The chlorine needed for making chloracetic acid and anthranilic acid (above), is generated electrolytically,[1] and purified by liquefaction. 10,000,000 pounds of salt are consumed for this purpose (the contents of more than 37,000,000 gallons of sea-water, or of a cube of sea-water 368 feet on edge).

By fusing the last-named product (phenylglycocollcarboxylic acid) with caustic soda, two products may be obtained, according to conditions: indoxyl (I), or indoxylic acid (II):

[1] Assuming an average current yield, 9,500,000 kilowatts or a steady consumption of 350 H. P., every second of the year are required for this process.

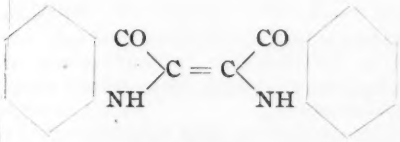


I.



II.

These, when oxidized by air in presence of alkalies, pass into indigo:



The present annual production of synthetic indigo has not been given to the public, but from the data obtainable it cannot be far from 3,000,000 pounds—about one-fourth of the world's supply. It is going to be a question of business rather than of manufacture when the indigo factories will have supplanted the indigo fields. Some of the above calculations will give a faint idea of the purely commercial side of this stupendous undertaking. The "Badische" has already invested over $4,500,000 in the plant and preliminary experiments.

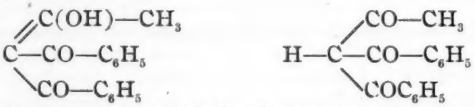
THE NEW ORGANIC CHEMISTRY.

The investigations we have just passed in rapid review have this in common, that they belong to the established order of things, and offer novelty chiefly in facts, hardly at all in principle. There is a newer organic chemistry in the air, however, just as there are a newer inorganic and a newer physical chemistry; and the developments of the newer organic chemistry are likely to be as startling as those of the older branches. The new organic chemistry at present tends in two directions, both of which shall engage our attention for a few minutes. The one is comprehended under the phenomena of tautomerism; the other deals with the chemistry of those elements other than carbon which enter into organic compounds.

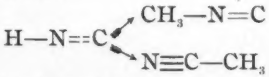
Tautomerism and its allied phenomena constitute one of the most difficult subjects of experimental science. Perhaps it will be best to give first of all a résumé of the nomenclature adopted by most of the investigators concerned in this work. By tautomerism in general, chemists have been accustomed to mean the ability of a single substance to behave as if it had two or more different structures, or to give derivatives belonging in two or more different classes. The closer investigation of these cases has

shown that a much more careful method of classifying the facts is necessary.[1]

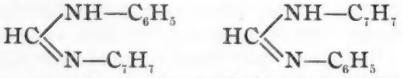
When two or more substances exist, so closely related that they pass into each other spontaneously, or upon very slight provocation (stereoisomerism being excluded), we speak of desmotropy; *e. g.*, dibenzoylacetyl methane, which forms the desmotropic isomers :[2]



If we have two sets of derivatives, but only one mother-substance extant in the free state, we have a case of tautomerism proper; *e. g.*, hydrocyanic acid, from which we can obtain two distinct series of esters :



A similar tautomerism exists in the case of the amidines; *e. g.*, phenyltolyl formamidine, which behaves as if it possessed both of the following formulas :



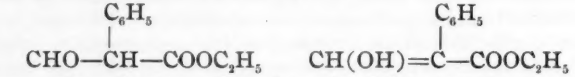
Such a case, where both tautomeric forms possess identical chemical character, is described as virtual tautomerism. Functional tautomerism exists where the (two) forms have different chemical character, as with acetoacetic ester; this reacts as a ketone,

$$CH_3—CO—CH_2—CO—OC_2H_5 \text{ keto form,}$$

and as an unsaturated alcohol,

$$CH_3—C(OH)=CH—CO—OC_2H_5 \text{ enol form.}$$

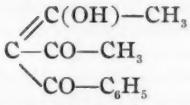
Desmotropic isomers tend to change into each other upon fusion, upon solution, in various solvents, etc.; in nearly all instances, a condition of equilibrium is finally reached, when we have the isomers present at the same time. This condition is known as allelotropy. An example is found in Wislicenus' phenylformylacetic ether, which upon solution in alcohol or in chloroform forms an allelotropic mixture of the two forms :



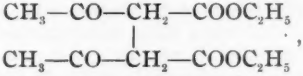
It sometimes happens that of a pair of desmotropic substances, the conditions of equilibrium are such that one can exist only in

[1] *Cf.* Rabe: *Ann. Chem.* (Liebig), **313**, 129 (1900).
[2] *Cf.* Claisen: *Ibid.*, **291**, 25 (1896).

traces: this limiting case of desmotropy is called pseudomerism; *e. g.*, benzoyldiacetylmethane:[1]

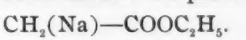


The investigation and definition of substances in this category is an exceedingly tedious and difficult affair. Without going into details, one citation will suffice. Diacetosuccinic ester,

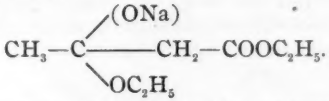


can exist in no less than thirteen different forms, of which Knorr has already described five.[2]

The question of tautomerism calls to mind the old battle-ground of acetoacetic ether. I have no desire to open old wounds, and so will cite only one publication dealing with this vexed question. Michael disagrees with Claisen's commonly accepted theory of the synthesis of acetoacetic ether (the addition of sodium ethylate to acetic ether, with subsequent condensation and elimination of alcohol), because metallic sodium acts upon acetic ether so much better than sodium ethylate. Michael thinks the primary formation of sodium acetic ether much more probable,[3]



This unsaturated compound then adds a molecule of unchanged acetic ester,



We cannot do more than refer to the tautomerism of the acid amides[4]

and to that of the oxyazo compounds, which seem to be either phenols or quinone-hydrazones according to circumstances.[5] In these cases, as in many others, two general rules must ever be kept in mind: One that generalizations are misleading, and that each case must be investigated upon its own merits,[6] the

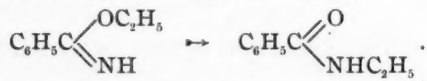
[1] *Cf.* Knorr: *Ann. Chem.* (Liebig), **306**, 350 (1899).
[2] *Ibid.*, **306**, 332 (1899).
[3] *Cf. Ber. d. chem. Ges.*, **33**, 3731 (1900).
[4] *Cf.* Titherley: *J. Chem. Soc.*, **79**, 391 (1901).
[5] *Cf.* McPherson: *Am. Chem. J.*, **25**, 485 (1901).
[6] *Cf.* Claisen: *Ann. Chem.* (Liebig), **291**, 45 (1896).

other that the metal derivatives (salts) of tautomeric and desmotropic forms are almost always constituted with their metal attached to oxygen when that is possible. This latter rule, laid down by Michael, was formally approved by no less an authority than Baeyer a short time ago.[1]

This theory of Michael's was recently elaborated and developed by Hantzsch, in connection with the latter's investigation of the diazo compounds.[2] In order to determine which of the two possible structures a tautomeric compound may have, Hantzsch shows that if one form may be acid in character the diagnosis is easy. If the given substance have the acid formula, it will be an electrolyte, and will form salts instantaneously; if it possess the neutral formula, it will (usually) be a non-conductor, and it forms salts with measurable velocity. It was this theory that led Hantzsch to revise his erstwhile views of the isodiazo compounds.[3]

Differing from tautomerism in outward appearance, yet closely related in their internal mechanism, are those reactions for which we possess no good English name. The Germans call them "Umlagerungen;" we are obliged to use the much more awkward term "molecular rearrangements." Fittig has long been engaged in studying the rearrangements occurring in unsaturated acids. The double bond in these acids seems to migrate from one part of the molecule under conditions that do not admit of prophecy,[4] so that in spite of the enormous amount of labor devoted to this investigation by Fittig and his pupils, no reliable generalizations can be drawn of the behavior of these substances.

Interesting rearrangements have been studied by H. L. Wheeler and his pupils.[5] These deal with the changes occurring in various acid amide derivatives. To cite only one example, phenylformimido ether is easily isomerized into ethyl benzamide,



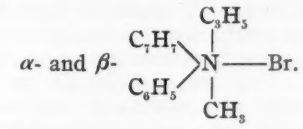
Time will not permit of more than a reference to Bamberger's study of the rearrangements of aromatic nitrogen compounds; *e. g.*, phenylhydroxylamine[6] forms a complex mixture of products on treatment with acids or alkalies. Bamberger assumes the intermediate existence of compounds with univalent nitrogen.

The second phase of the new organic chemistry is still in its beginnings. While the chemistry of carbon in its organic derivatives is by no means exhausted, an ever-increasing army of in-

[1] *Ber. d. chem. Ges.*, **33**, Sonderheft, p. 64 (1900).
[2] *Cf.* above.
[3] *Cf. Ber. d. chem. Ges.*, **32**, 575 (1899).
[4] *Ann. Chem.* (Liebig), **304**, 117 (1899).
[5] *Am. Chem. J.*, **23**, 135 (1900).
[6] *Ber. d. chem. Ges.*, **33**, 3600 (1900).

vestigators is devoting itself to the study of the other elements which enter into organic compounds. To be sure, we have long been aware of the development of "nitrogen chemistry;" but the peculiarities of nitrogen in its numerous compounds have been so intimately bound up with the history and progress of carbon chemistry proper, that we have not been conscious of any sharp line of demarcation. But now that we are beginning to be interested in the welfare of the carbon derivatives of other elements, the time seems ripe for a systematic attempt to "organize" inorganic chemistry; *i. e.*, to study the inorganic elements as carbon has been studied. Much valuable material has already been collected for this purpose.

During the past year or two, much interest has been accorded the stereochemistry of other elements. It is hardly necessary to recall the tremendous influence that the theories of van't Hoff and LeBel have had on the growth of carbon chemistry during the past twenty years. LeBel himself extended his studies to nitrogen, and had succeeded in obtaining an asymmetric nitrogen compound possessing optical activity.[1] To be sure, there was considerable skepticism about LeBel's results, until he showed that the greatest care is necessary in separating the optical isomers by fermentation, the method he had adopted. How quickly our views on such things change! Only two years ago Marckwald published some work to prove conclusively that these so-called isomers could not be separated.[2] To-day a dozen groups of isomers have been carefully studied. There was needed only the proper reagent. This was found by W. J. Pope in camphor sulphonic acid, $C_{10}H_{15}O.SO_3H$.[3] A short time before, Wedekind[4] had prepared two isomeric forms of a substituted ammonium salt; *viz.*, benzylphenylallylmethyl ammonium bromide (and iodide),

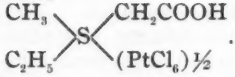


These isomers were inactive. Pope succeeded in separating the α-form into two optically active modifications, turning polarized light to the right and to the left almost equally ($[\alpha]_D + 68.6°$ and $-67.3°$). Pope has since then prepared numerous other active ammonium compounds.

The sulphur atom also has the power of becoming asymmetric. Pope and Peachey[5] have isolated an optically active *d*-methyl-

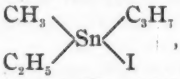
[1] *Compt. rend.*, **112**, 724 (1891).
[2] *Ber. d. chem. Ges.*, **32**, 560 (1899).
[3] *J. Chem. Soc.*, **78**, 1127 (1900).
[4] *Ber. d. chem. Ges.*, **32**, 517 (1899).
[5] *Loc. cit.*, p. 1072.

ethylthetin chlorplatinate,



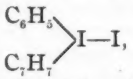
The asymmetric sulphur atom is easily racemized; *i. e.*, rendered inactive by isomerization of half the molecules present.

Tin, an element resembling carbon and sulphur in that it can become quadrivalent, may also be rendered asymmetric and optically active.[1] Methylethylpropyl stannic iodide,



is an oil, and is dextrorotatory. The chief peculiarity of this asymmetric tin atom, however, is that no laevorotatory modification exists. As fast as the dextro form separates, the remaining laevo racemizes itself, thus forming fresh dextro, which alone separates. By completely evaporating the solution to dryness, the whole of the previously inactive salt is converted into its dextrorotatory isomer. This fact is of great significance for the future of stereochemistry.

Efforts to render the iodine atom in iodonium compounds asymmetric have proved abortive so far.[2] Phenyltolyliodonium iodide,



could not be rendered optically active.

It is to be expected that molecular asymmetry will be discovered in a great many other elements. Numerous elements are capable of combining with carbon radicals, and many curious compounds have resulted. We cannot do more at this time than refer to the extensive studies that Michaelis has been carrying on for years with the organic derivatives of selenium, tellurium, phosphorus, boron, silicon, etc. Michaelis has recently told us his motive in this work. He points out[3] that the type theory, to which organic chemistry has owed so much of her early progress, has been deserted by the modern "organiker." His own work has been carried on for the express purpose of developing this theory, which he hopes will eventually lead to an insight into the real laws of combination.

Quite a number of new mercury compounds of organic radicals have been prepared recently, a number of investigators apparently stumbling upon them at about the same time. Thus, Dimroth[4] has found that aromatic compounds generally easily replace

[1] *Proc. Chem. Soc.*, **16**, 42 (1900).
[2] Kipping and Peters: *Proc. Chem. Soc.*, **16**, 62 (1900).
[3] *Ann. Chem.* (Liebig), **314**, 276 (1901).
[4] *Ber. d. chem. Ges.*, **31**, 2154 (1898); **32**, 758 (1899).

one or more hydrogen atoms by univalent mercury radicals; a different class of aromatic quicksilver compounds related to benzoic acid are described by Pesci;[1] whereas Hofmann and his pupils[2] have found that in the fatty series four different types of substitution of mercury for hydrogen can be distinguished.

Even the chemistry of so well-known an element as oxygen has been greatly extended by the organic chemist within the last few years. One important topic, though outside the lines of organic chemistry proper, may be alluded to. The phenomena of auto-oxidation have excited much interest. Many substances which are absolutely indifferent towards free oxygen (moist or dry) are easily oxidized in the presence of certain other substances. In many instances, these "contact-substances" or catalyzers are themselves oxidized at the same time. In other cases, they remain unchanged. The exact mechanism of auto-oxidation still needs very careful study, in which Manchot[3] has made an excellent beginning. Hydrogen peroxide often plays an important part in these reactions as an intermediate product. In other cases, again, Baeyer and Villiger have been able to demonstrate the intermediate formation of complex organic hyperoxides;[4] thus benzaldehyde, which in moist air is oxidized to benzoic acid, first takes up a molecule of oxygen, forming benzoyl hydroperoxide,

$$C_6H_5CHO + O = C_6H_5CO-O-OH.$$

This will oxidize a second molecule of benzaldehyde,

$$\begin{matrix} C_6H_5CO-O-OH \\ C_6H_5CHO \end{matrix} + = \begin{matrix} C_6H_5CO-OH \\ C_6H_5CO-OH \end{matrix} + H_2O,$$

but other substances are usually oxidized first if they are present.

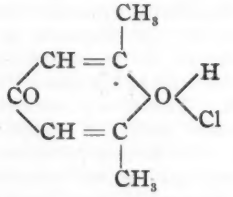
Baeyer and Villiger have also prepared mono- and diethyl-hydrogen peroxide. The former, preferably called ethyl hydroperoxide, is easily prepared by action of hydrogen peroxide upon ethyl sulphate. It has the formula C_2H_5-O-OH, is fairly stable, and differs from its mother-substance hydrogen peroxide (now called hydroperoxide) in possessing no reducing properties whatever; it is merely an oxidizing agent.[5]

The same chemists obtained diethyl-peroxide from the same reagents in different proportions. It has the formula $C_2H_5-O-O-C_2H_5$; it has neither oxidizing nor reducing properties. Reducing agents convert it into alcohol. From the behavior of these two compounds Baeyer thinks that hydrogen peroxide itself has the old formula HO—OH; the existence of

[1] *Atti dei Lincei Roma*, (5), **9**, 255 (1900).
[2] *Cf. Ber. d. chem. Ges.*, **33**, 1328-1364.
Cf. Ztschr. anorg. Chem., **27**, 397 (1901).
[4] *Ber. d. chem. Ges.*, **33**, 1581 (1900).
[5] *Ibid.*, **34**, 738 (1901).

quadrivalent oxygen in its molecule, as in the suggested formula $\begin{matrix} H \\ H \end{matrix}\!\!>\!O=O$, appears to be excluded.[1]

But although hydroperoxide may not contain quadrivalent oxygen, the fact that oxygen does become quadrivalent in some of its compounds has been established by Collie and Tickle.[2] Dimethyl-pyrone forms salts with various hal-hydric acids; *e. g.*, the hydrochlorate



These salts behave like the salts of a very weak base, and are completely hydrolyzed in dilute aqueous solution. If the addition of hydrochloric acid had occurred within the carbon ring, this hydrolysis would not manifest itself.

Oxygen owes its name to its strong acid-forming tendencies. We should expect that as we increase the amount of oxygen in a given molecule, the acid properties of that molecule would show a proportional augmentation. But such does not seem to be the case. If in benzoic acid, $C_6H_5CO—OH$, we introduce a third oxygen atom in the place where it ought to have the greatest acidifying influence (*viz.*, in the carboxyl group itself, $C_6H_5CO—O—OH$), the resulting compound (benzoyl hydroperoxide) is not only less acid than benzoic acid, but is actually weaker than carbonic acid.[3] It would have been difficult to foresee this.

SOME NEW ORGANIC THEORIES.

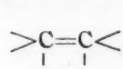
Time and space will not permit more than a brief reference to the recent endeavors to extend our fundamental conceptions of organic processes. For many years, chemists have been content to study organic chemistry with attention fixed chiefly upon matters of detail. The larger aspects of the subject have lain dormant until quite recently. During the last few years, however, an effort has been made on several sides to replace some of our theoretical views by others better suited to present conditions. For it must not be concealed that many investigators are dissatisfied with structural and with stereochemical methods of explana-

[1] *Ber. d. chem. Ges.*, **33**, 3392 (1900).
[2] *J. Chem. Soc.*, **75**, 710 (1899).
[3] Baeyer-Villiger: *Ber. d. chem. Ges.*, **33**, 1569 (1900).

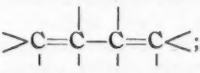
tion, dissatisfied with the idea of valence, aye, even with the atomic theory itself.[1]

In the nature of things, all recent and untried theories meet with opposition; they are often crude in detail, sometimes in error as to facts; and for our present purposes it will be better to sketch in a few words what the theorists are hoping to achieve rather than attempt to weigh what they have actually accomplished. Organic chemistry is in no urgent need of new guide-posts (witness the mass of new material each year), so that our caution is at least pardonable.

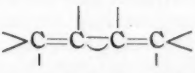
A comprehensive theory of unsaturated compounds has been attempted by Thiele.[2] His fundamental idea is that in the so-called double bond the carbon atoms are really united by two valence units each, but that a small amount of "residual affinity" is left:



It is this residual affinity that gives to the double bond its additive power; as addition occurs, more residual affinity is liberated, owing to a sort of equilibrium condition. In the case of two adjacent double bonds, two pairs of residual affinities would exist,



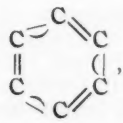
but the central pair neutralize each other, just as two magnet bars would, and we have residual affinity left only at the extreme ends of such a "conjugated system of double bonds" as Thiele calls it:



In this way he seeks to explain the actual fact that where such a pair of double bonds occurs within a molecule, addition takes place only at the outer ends, with the establishment of a new double bond:

$$H_2C{=}CH{-}CH{=}CH_2 + Br_2 = BrH_2C{-}CH{=}CH{-}CH_2Br.$$

Applied to benzene, this theory shows us three conjugated double bonds,



and many of the peculiarities of benzene can be brought into rela-

[1] *Cf.* Ostwald's "Text-book of Inorganic Chemistry."

[2] *Ann. Chem.* (Liebig), **306**, 87 (1899).

tion to the properties of other unsaturated compounds. Thiele has found a supporter in Baeyer,[1] who declares that here we have the "final expression" of thirty years of discussion. As we owe the bulk of our knowledge of the benzene ring to Baeyer, this sounds encouraging.

An entirely different method of explaining organic reactions and additions has been elaborated by Nef;[2] according to him, organic compounds have an irresistible tendency to become strongly unsaturated, with formation of bivalent carbon; *e. g.*,

$$CH_3CH_2OH \rightarrow CH_3—CH\langle + H_2O,$$

and an equally irresistible tendency to pass back again to the saturated, quadrivalent condition by adding on any molecules that may be within reach; *e. g.*,

$$CH_3—CH\langle + CH_3CH_2OH = CH_3—CH\langle^{H}_{O—CH_2—CH_3}.$$

What is missed in Nef's theory is the motive; it is often difficult to see why some other form of addition does not occur when a number of different, available molecules are present. Nef's views have not found the support that has been accorded to Thiele's theory.

Finally, a third course of reasoning has been developed by Michael.[3] Michael's theory is too recent, too complicated and too extensive to permit of any properly comprehensive summary. In its essence, it ascribes to every atom in the molecule a polarity (which is expressed in electric terms); addition reactions are caused by attempts to neutralize this polarity; and the polarity of each atom is modified more or less profoundly by the presence and polarity of all the other atoms in the molecule. With reference to the theories of Thiele and Nef, Michael endeavors to show that Nef's views do not agree with the facts, whereas all of Thiele's deductions can be drawn from his own,—these being more general and more fundamental. If I may append my personal opinion of these three theories, I should venture the prediction that Michael's is more likely to grow into the needs of organic chemistry than either of the others.

CONCLUSION.

It will be seen that the prospects of organic chemistry are as bright as ever. At each of the older problems hosts of busy workers are successfully laboring. New problems are constantly arising, and new methods of experimentation are being as steadily devised for their study. A healthy and skeptical criticism is being accorded our present theories; and from the constructive side

[1] *Ber. d. chem. Ges.*, **33**, Sonderheft, p. 63 (1900).
[2] *Ann. Chem.* (Liebig), **298**, 202 (1897).
[3] *J. prakt. Chem.*, **60**, pp. 1–178 (1899).

efforts are not lacking to provide us with more accurate and more comprehensive generalizations. From within and without, the organic chemist is stimulated to his best endeavors; his efforts are encouraged, and his achievements are appreciated. The scientist can ask no more.

To him, however, busy with other work, who gazes occasionally on organic chemistry, it may often seem to lack coherence of effort, to waste its strength burrowing for details, and to owe many of its successes to mere chance. If such a one there be, I recommend to his attention a notable address by Baeyer last year.[1] From this address he will learn of the unity of research work—that nearly all of this master's brilliant discoveries were due not to luck or chance, but to the consistent prosecution of a logical train of ideas. Baeyer's first extensive research work dealt with uric acid. The similarity of alloxan and isatin led him to the indigo group. From this sprang the tension theory, the quinoline synthesis, and tautomerism. The tension theory led to the curious tetra-acetylene dicarboxylic acid; this to the benzene ring studies. The investigation of terpenes and related substances took its rise from their similarity to reduction products of benzene. During the terpene researches some curious peroxides were obtained, and the work described above (on ethyl hydroperoxide, etc.) resulted from following up these latter. Thus we can trace Baeyer's research work—than whom no single man has contributed more to the stupendous growth of organic chemistry—back in an unbroken logical chain extending over forty years.

There lies here a world of thought for him who cares to find it.

ARTHUR LACHMAN.

NOTE.

A Gravimetric Method for the Estimation of Hydrogen Dioxide.—All the methods thus far described for the estimation of hydrogen dioxide are volumetric, which may be divided into the three following classes: first, gasometry, by the use of Lunge's nitrometer, or some modification of it; second, iodometry, originated by Kingzett, and depends upon the liberation of iodine from potassium iodide in the presence of sulphuric acid; and, third, oxidimetry, the mutual decomposition of potassium permanganate and hydrogen dioxide in the presence of sulphuric acid. Of these three methods, the latter is preferred and most frequently used. The author has obtained good results by estimating the hydrogen dioxide as water. For the purpose a "Schrötter" apparatus (with tube and glass stoppers), such as used for carbon

[1] *Ber. d. chem. Ges.*, **33**, Sonderheft, p. 52ff. (1900).

dioxide determinations in mineral carbonates, was employed. The drying tube was half filled with concentrated sulphuric acid and the "acid tube" with a solution of potassium permanganate (2 grams in 100 cc. water). The bulb contained 10 cc. water and 5 cc. of dilute sulphuric acid (1 : 5). The weight of the apparatus was now noted and then about 1 cc. of the hydrogen dioxide was introduced. The apparatus was again weighed to insure the amount of hydrogen dioxide added. The permanganate was now allowed to flow in drop by drop until a permanent faint rose tint was formed. The apparatus was next allowed to cool and then weighed. The author claims that if the usual precautions are exercised, as prescribed in carbon dioxide determinations, excellent results can be obtained. However, it must be remembered that the loss in weight must be divided by 2, because one-half of the oxygen comes from the permanganate itself, and, furthermore, a too great excess of the latter must be avoided because the sulphuric acid decomposes it, giving off oxygen, thus leading to higher results.

GEORGE E. HOSCH.

NEW BOOKS.

JAHRBUCH DES VEREINS DER SPIRITUS-FABRIKANTEN IN DEUTSCHLAND. Erster Band, 1901. Berlin : Paul Parey. 316 pp. Price, 6 M.

This volume gives reports of the work of the German Society of Alcohol Distillers, also of the Society of Starch Manufacturers, for 1900 and is the first of the series. Heretofore the minutes and reports of these organizations have been published in the form of a supplement number to the *Zeitschrift für Spiritusindustrie*. This first volume of the new yearbook contains 316 pages and presents not only the proceedings of the two societies but also a large amount of statistical matter relating to production and consumption of alcohol and starch. The first-named society supports a number of experimental laboratories, and the investigations of these are briefly described in the book. As alcohol may be used in the arts in Germany tax-free under certain restrictions, space is devoted to a discussion of new outlets for alcohol in various directions. The chapter relating to the advantages of the alcohol motor presents some very interesting data and is one of the best in the book.

J. H. LONG.

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PROCEEDINGS

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